

C24	0.8990 (7)	0.1075 (5)	0.6557 (7)	0.133 (3)
C25	0.9461 (6)	0.0841 (5)	0.5737 (7)	0.132 (3)
C26	0.9244 (5)	0.1103 (4)	0.4776 (6)	0.101 (2)
N1'	0.8730 (3)	-0.2973 (3)	0.5414 (4)	0.095 (2)
C2'	0.8879 (4)	-0.3634 (4)	0.5898 (5)	0.104 (2)
N3'	0.8133 (4)	-0.3951 (3)	0.6259 (4)	0.094 (2)
C4'	0.7366 (4)	-0.3867 (3)	0.5813 (4)	0.076 (2)
C5'	0.7319 (3)	-0.3327 (3)	0.5097 (4)	0.069 (1)
N5'	0.6619 (3)	-0.3043 (2)	0.4546 (3)	0.063 (1)
C6'	0.5770 (4)	-0.3239 (3)	0.4432 (4)	0.079 (2)
C7'	0.5235 (3)	-0.2857 (3)	0.3835 (4)	0.084 (2)
C8'	0.5557 (4)	-0.2264 (3)	0.3324 (4)	0.089 (2)
N9'	0.6402 (3)	-0.2083 (2)	0.3486 (3)	0.073 (1)
C9'	0.6925 (3)	-0.2470 (3)	0.4094 (4)	0.063 (2)
N10'	0.7743 (3)	-0.2346 (2)	0.4306 (3)	0.073 (1)
C10'	0.7966 (3)	-0.2888 (3)	0.4934 (4)	0.069 (1)
C11'	0.9471 (4)	-0.2557 (3)	0.5172 (5)	0.113 (2)
C12'	0.8296 (5)	-0.4503 (4)	0.6999 (6)	0.150 (3)
O13'	0.6752 (3)	-0.4236 (2)	0.6034 (3)	0.101 (1)
O14'	0.5563 (2)	-0.3824 (2)	0.4924 (3)	0.104 (1)
C15'	0.4281 (5)	-0.3009 (4)	0.3807 (6)	0.125 (3)
C16'	0.3939 (6)	-0.3224 (5)	0.2814 (6)	0.174 (4)
C17'	0.3919 (6)	-0.3894 (5)	0.2472 (7)	0.198 (5)
C18'	0.3596 (7)	-0.4120 (5)	0.1459 (8)	0.204 (5)
O19'	0.5104 (3)	-0.1897 (2)	0.2758 (3)	0.125 (2)
C20'	0.6734 (4)	-0.1469 (3)	0.2981 (4)	0.086 (2)
C21'	0.6654 (4)	-0.0808 (3)	0.3610 (4)	0.077 (2)
C22'	0.7346 (5)	-0.0572 (3)	0.4210 (5)	0.104 (2)
C23'	0.7256 (7)	0.0025 (4)	0.4768 (6)	0.130 (3)
C24'	0.6535 (8)	0.0380 (4)	0.4761 (6)	0.131 (3)
C25'	0.5858 (6)	0.0148 (4)	0.4172 (7)	0.124 (3)
C26'	0.5926 (5)	-0.0453 (4)	0.3600 (5)	0.100 (2)

Table 2. Selected geometric parameters (Å, °)

C4—O13	1.245 (8)	C4'—O13'	1.244 (8)
C6—O14	1.331 (7)	C6'—O14'	1.348 (7)
C16—C17	1.364 (16)	C16'—C17'	1.369 (14)
C15—C16—C17	131.3 (10)	C15'—C16'—C17'	124.6 (8)
C16—C17—C18	118.8 (10)	C16'—C17'—C18'	125.4 (9)
C6—C7—C15—C16	91.5 (8)		
C8—C7—C15—C16	-87.9 (8)		
C8—N9—C20—C21	93.2 (6)		
C9—N9—C20—C21	-89.1 (6)		
C7—C15—C16—C17	-114.3 (12)		
C15—C16—C17—C18	-9.0 (18)		
N9—C20—C21—C22	-69.4 (8)		
N9—C20—C21—C26	112.5 (7)		
C6'—C7'—C15'—C16'	-117.7 (7)		
C8'—C7'—C15'—C16'	69.4 (8)		
C8'—N9'—C20'—C21'	90.4 (6)		
C9'—N9'—C20'—C21'	-90.4 (6)		
C7'—C15'—C16'—C17'	87.6 (10)		
C15'—C16'—C17'—C18'	-178.3 (9)		
N9'—C20'—C21'—C22'	96.8 (7)		
N9'—C20'—C21'—C26'	-82.8 (7)		

The structure of (I) was solved by direct methods using *MULTAN78* (Main *et al.*, 1978) with $E > 1.47$. The phase set with best combined figure of merit was used in computing the E map. The full structure (two molecules in the asymmetric unit) was obtained from this map. Full-matrix least-squares anisotropic refinement of the non-H atoms was carried out with *SHELX76* (Sheldrick, 1976). Atoms C15, C16, C17 and C18 of both molecules have increasingly large displacement parameters. H atoms were calculated and allowed to ride on their parent atoms, but those attached to the O14 and O14' atoms could not be located.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Acetyl-6-bromocoumarin

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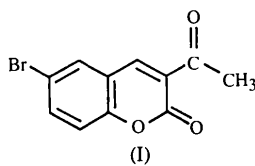
Abstract

The crystal structure of the title compound, C₁₁H₇BrO₃, has been determined using 1549 observed reflections with $I > 2.5\sigma(I)$. The coumarin moiety is planar and makes a dihedral angle of 6.6(4)° with the mean plane of the acetyl group attached to C(3). The molecules adopt the *S-cis* configuration in the crystal and are linked by weak C—H···O interactions.

Comment

Coumarins with various substituents at position 3 have been found to exhibit a variety of biological properties (Feurer, 1974) and are of spectroscopic interest (Clinging, Dean & Houghton, 1970). 3-Acetylcoumarins have

been reported to have antimicrobial properties (Ishii, 1952) and are useful synthons for coumarin analogs of chloramphenicol (Bevinakatti & Badiger, 1980) and 3-coumarinyl thiazoles (Panigrahi & Raut, 1971). In view of the biological importance of the compound and as a continuation of the structure analysis of coumarin derivatives (Vasudevan, Puttaraja & Kulkarni, 1990, 1991) the determination of the structure of the title compound, (I), has been undertaken.



A plot of the molecule is shown in Fig. 1. The phenyl ring of the coumarin moiety is highly planar compared to the pyrone ring and makes a dihedral angle of $1.5(3)^\circ$ with the mean plane of the pyrone ring. The coumarin

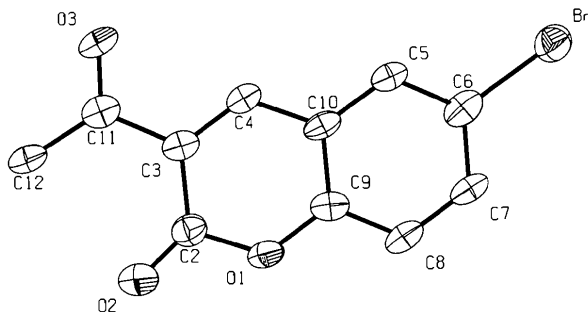


Fig. 1. The structure of the title molecule with 50% probability displacement ellipsoids. H atoms are omitted.

moiety is almost planar, with the Br atom displaced from the least-squares plane by $0.070(8) \text{ \AA}$. The acetyl group is planar and makes a dihedral angle of $6.0(4)^\circ$ with the mean plane of the pyrone ring and $6.6(4)^\circ$ with the mean plane of the coumarin moiety.

The bonds $\text{O}(1)\text{—C}(2)$ [$1.422(10) \text{ \AA}$] and $\text{O}(1)\text{—C}(9)$ [$1.419(10) \text{ \AA}$] are nearly equal in length, but slightly longer (by 6σ) than the analogous bonds in 3,3'-methylenebis(6-bromo-4-hydroxycoumarin) (Alcock & Hough, 1972). The bonds $\text{C}(3)\text{—C}(4)$ [$1.394(11) \text{ \AA}$] and $\text{C}(2)\text{—O}(2)$ [$1.249(10) \text{ \AA}$] are longer than previously reported (Shimizu, Kashino & Haisa, 1975; Vasudevan, Puttaraja & Kulkarni, 1991) but show double-bond character. Comparison of the $\text{C}(3)\text{—C}(4)$ bond length with that in other coumarin derivatives indicates that this bond length varies from 1.30 to 1.41 \AA depending on the groups attached at $\text{C}(3)$ or $\text{C}(4)$ (Shimizu *et al.*, 1975).

The bond angles around $\text{C}(6)$ [$\text{Br—C}(6)\text{—C}(5)$ $121.8(6)$, $\text{Br—C}(6)\text{—C}(7)$ $121.1(6)$ and $\text{C}(5)\text{—C}(6)\text{—C}(7)$ $117.0(7)^\circ$] show variations compared to those reported for 3,3'-methylenebis(6-bromo-4-hydroxycoumarin) by Alcock & Hough (1972) [$118.2(6)$, $120.1(7)$ and $121.8(9)^\circ$, respectively]; this might be a result of the longer $\text{Br—C}(6)$ distance in (I).

The angles around $\text{C}(2)$ in (I) are $119.9(7)$, $112.8(7)$ and $127.4(7)^\circ$, compared with $117.3(3)$, $117.2(3)$ and $127.4(7)^\circ$ in coumarin (Gavuzzo, Mazza & Giglio, 1974), and resemble the geometry of a carboxylic group; $\text{O}(2)\text{—C}(2)\text{—O}(1)$ [$119.9(7)^\circ$] is smaller than $\text{O}(2)\text{—C}(2)\text{—C}(3)$ [$127.4(3)^\circ$], which may result from the steric effect of the substituent at $\text{C}(3)$. The $\text{C}(3)$ carbonyl group is coplanar with the coumarin moiety [$\text{C}(4)\text{—C}(3)\text{—C}(11)\text{—O}(3)$ $-4.2(1.0)^\circ$] and is

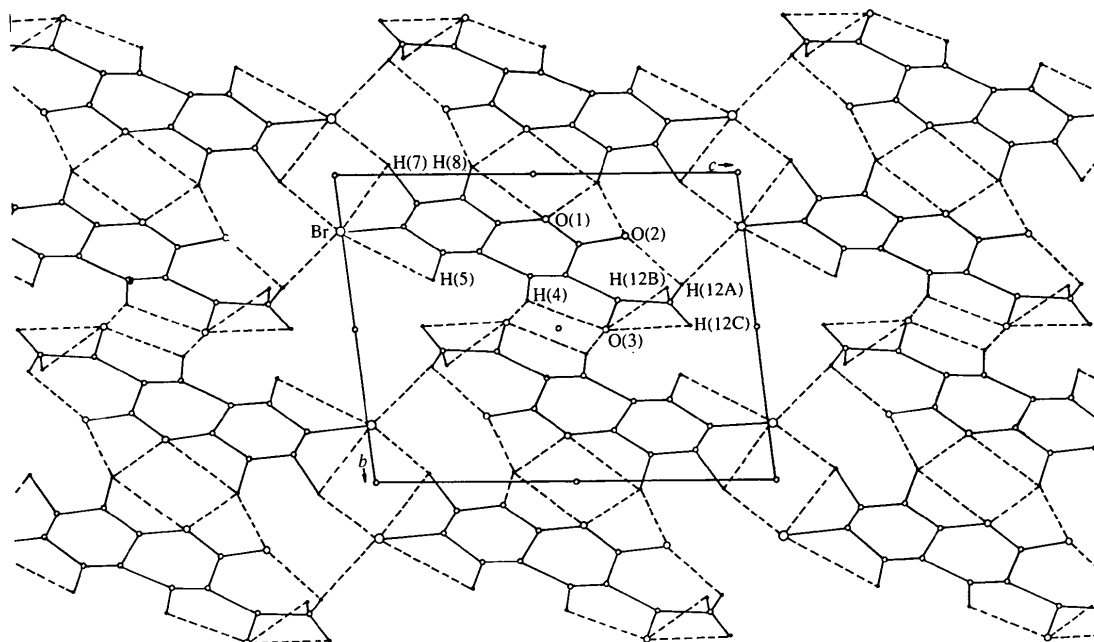


Fig. 2. The molecular packing viewed down the *a* axis.

cis to C(3)—C(4) about the C(3)—C(11) bond. This allows maximum separation of O(2) and O(3), which is reflected in the increased bond angles O(2)—C(2)—C(3) [127.4 (7)°] and C(12)—C(11)—C(3) [125.1 (7)°] and also keeps electronic repulsion to a minimum. The high value of the exocyclic C(3)—C(11) bond length [1.540 (11) Å] compared to the length of a normal C_{sp²}—C_{sp²} bond [1.487 Å] may be due to σ -electron delocalization.

The view of the crystal packing shown in Fig. 2 indicates that the orientation of O(3) and H(4) is almost *peri*. The intramolecular distance is 2.43 (5) Å. The corresponding intermolecular distance [2.52 (5) Å] indicates that the packing is stabilized by such C—H...O interactions, which can be considered as weak hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984).

Experimental

Crystals of (I) were supplied by MVK.

Crystal data

C₁₁H₇BrO₃

M_r = 267.08

Triclinic

P $\bar{1}$

a = 4.029 (1) Å

b = 11.125 (2) Å

c = 11.775 (1) Å

α = 97.339 (9)°

β = 99.948 (9)°

γ = 90.040 (10)°

V = 515.45 (16) Å³

Z = 2

D_x = 1.721 Mg m⁻³

D_m = 1.70 Mg m⁻³

D_m measured by flotation in KI solution

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 20–25°

μ = 3.93 mm⁻¹

T = 300 K

Prism

0.2 × 0.2 × 0.2 mm

Pale yellow

θ_{\max} = 32.5°

h = -4 → 4

k = 0 → 13

l = -13 → 13

3 standard reflections

monitored every 100

reflections

intensity decay:

insignificant

Refinement

Refinement on *F*

R = 0.067

wR = 0.067

S = 1.298

(Δ/σ)_{max} = 0.05

$\Delta\rho_{\max}$ = 1.61 e Å⁻³

$\Delta\rho_{\min}$ = -1.27 e Å⁻³

Extinction correction: none

1549 reflections
164 parameters
All H-atom parameters
refined
w = 1/ σ^2 (*F*)

Atomic scattering factors
from Cromer & Mann
(1968) and Stewart,
Davidson & Simpson
(1965)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Br	0.4042 (3)	0.1829 (1)	0.0091 (1)	3.9 (1)
O(1)	0.2884 (14)	0.1402 (4)	0.5298 (5)	3.1 (3)
O(2)	0.3449 (16)	0.2080 (5)	0.7264 (5)	4.3 (3)
O(3)	0.9588 (17)	0.4945 (5)	0.6763 (5)	4.5 (3)
C(2)	0.410 (2)	0.2249 (7)	0.6296 (7)	2.9 (4)
C(3)	0.6096 (19)	0.3262 (7)	0.6029 (7)	2.5 (4)
C(4)	0.638 (2)	0.3363 (6)	0.4881 (7)	2.6 (4)
C(5)	0.518 (2)	0.2595 (6)	0.2647 (7)	2.8 (4)
C(6)	0.3776 (19)	0.1683 (7)	0.1716 (7)	2.9 (4)
C(7)	0.209 (2)	0.0690 (7)	0.2013 (7)	3.0 (4)
C(8)	0.181 (2)	0.0597 (7)	0.3194 (7)	3.1 (4)
C(9)	0.321 (2)	0.1495 (7)	0.4131 (7)	2.6 (4)
C(10)	0.4940 (19)	0.2494 (6)	0.3862 (7)	2.5 (4)
C(11)	0.784 (2)	0.4187 (7)	0.7041 (7)	3.0 (4)
C(12)	0.746 (3)	0.4206 (8)	0.8332 (8)	4.8 (5)

Table 2. Selected geometric parameters (Å, °)

Br—C(6)	1.962 (8)	C(5)—C(6)	1.432 (11)
O(1)—C(2)	1.422 (10)	C(5)—C(10)	1.469 (11)
O(1)—C(9)	1.419 (10)	C(6)—C(7)	1.408 (11)
O(2)—C(2)	1.249 (10)	C(7)—C(8)	1.432 (12)
O(3)—C(11)	1.210 (10)	C(8)—C(9)	1.427 (11)
C(2)—C(3)	1.482 (11)	C(9)—C(10)	1.410 (11)
C(3)—C(4)	1.394 (11)	C(11)—C(12)	1.551 (11)
C(4)—C(10)	1.474 (11)	C(11)—C(3)	1.540 (11)
C(9)—O(1)—C(2)	127.0 (6)	C(6)—C(7)—C(8)	121.3 (7)
O(1)—C(2)—O(2)	119.9 (7)	C(7)—C(8)—C(9)	122.2 (7)
O(1)—C(2)—C(3)	112.8 (7)	C(8)—C(9)—C(10)	117.7 (7)
O(2)—C(2)—C(3)	127.4 (7)	C(8)—C(9)—O(1)	121.9 (7)
C(2)—C(3)—C(11)	118.6 (7)	C(10)—C(9)—O(1)	120.4 (7)
C(2)—C(3)—C(4)	120.1 (7)	C(4)—C(10)—C(5)	125.9 (6)
C(4)—C(3)—C(11)	121.3 (7)	C(4)—C(10)—C(9)	114.3 (7)
C(3)—C(4)—C(10)	125.2 (7)	C(5)—C(10)—C(9)	119.8 (7)
C(10)—C(5)—C(6)	121.8 (7)	C(3)—C(11)—C(12)	125.1 (7)
C(5)—C(6)—Br	121.8 (6)	C(3)—C(11)—O(3)	114.8 (7)
C(7)—C(6)—C(5)	117.0 (7)	C(12)—C(11)—O(3)	120.2 (7)
C(7)—C(6)—Br	121.1 (6)	C(12)—C(11)—C(3)	125.1 (7)

The atomic coordinates of the non-H atoms were determined by direct methods using *NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989) and refined with anisotropic displacement parameters. H atoms were located from difference Fourier maps except for the methyl H atoms, which were fixed from geometrical considerations, and refined with isotropic displacement parameters using *NRCVAX*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

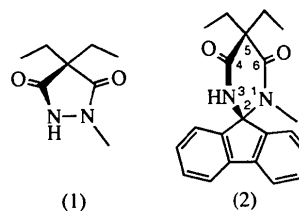
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Comment

Conformational studies of cyclic dipeptides by X-ray diffraction and ^1H NMR spectroscopy (Gdaniec & Liberek, 1986; Liberek & Bednarek, 1978) have demonstrated that piperazinedione rings tend to assume a boat conformation with side chains folding over the ring. Some cyclic dipeptides possessing a rigid conformation are considered to be potential catalysts for asymmetric syntheses (Tanaka, Mori & Inoue, 1990).

Cyclic retro-inverso dipeptides incorporate malonic acid residues into cyclic dipeptide analogues and reverse the direction of the peptide bond. ^1H NMR spectra and semiempirical energy calculations indicate that the most stable conformations of hexahydropyrimidinedione (HHPD) rings with two aromatic side chains are those in which the HHPD ring adopts a planar or a boat structure (Yamazaki, Nunami & Goodman, 1991). No X-ray structure of a hexahydropyrimidine-4,6-dione has been reported previously. Here we present the crystal structure of 5,5-diethyl-1-methyl-1*H*,2*H*,3*H*,5*H*-pyrimidine-2-spiro-9'-fluorene-4,6-dione, (2), which can be regarded as an insertion product of 9-fluorenylidene into the N—N bond of the pyrazolidinedione precursor 4,4-diethyl-1-methylpyrazolidine-3,5-dione, (1). Compound (2) was realised through a ring-expansion process following the reaction of (1) with 9-bromofluorene.



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5,5-Diethyl-1-methyl-1*H*,2*H*,3*H*,5*H*-pyrimidine-2-spiro-9'-fluorene-4,6-dione

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Abstract

The title compound, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$, was synthesized from the corresponding pyrazolidinedione precursor by 9-fluorenyl substitution and subsequent ring expansion. The hexahydropyrimidinedione (HHPD) ring has a very flattened chair conformation and is nearly perpendicular [$88.79(13)^\circ$] to the 2-spiro-9'-fluorene ring. The two ethyl groups adopt a folded conformation and lie on opposite sides of the HHPD ring. A hydrogen-bonding scheme consisting of $\text{N—H}\cdots\text{O}=\text{C}$ and $\text{C—H}\cdots\text{O}=\text{C}$ interactions produces parallel molecular layers.

An illustration of (2), together with the atom-numbering scheme, is shown in Fig. 1. An initial examination of the HHPD ring showed it to be nearly planar, the mean deviation from its least-squares plane being 0.018 \AA . However, a subsequent least-squares-plane calculation using only the central portion of the ring (N1, N3, C4 and C6) exhibits near perfect planarity (mean deviation 0.001 \AA) while the sp^3 -hybridized C2 and C5 atoms, located at opposite ends of the ring, deviate from the central portion by $-0.063(3)$ and $0.049(3)\text{ \AA}$, respectively. Thus, the HHPD conformation can be considered to be a flattened chair form. Torsion angles C2—N3—C4—C5 of $5.5(6)^\circ$ and C2—N1—C6—C5 of $-5.1(5)^\circ$ also illustrate this point. In addition, the N1 atom is slightly pyramidal as illustrated by the fact that C7 is $-0.064(5)\text{ \AA}$ out of the central portion of the HHPD ring plane and *cis* to the C2 atom. The position of H3 could not be determined with sufficient accuracy to characterize the N3 atom definitively as either trigonal planar or slightly pyramidal. Since hexahydropyrimidine itself has a flexible chair conformation and pyramidal N atoms (Armarego, 1977), the above results