Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.177$
$S = 1.091$
2213 reflections
338 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1412P)^2 + 0.1949P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.560$ e Å^{-3}
$\Delta\rho_{\min} = -0.511$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0073 (19)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.4 (4)

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

C9—N2	1.536 (5)	C15—N2	1.504 (6)
C10—N2	1.501 (6)		
O3—C3—C2	124.3 (5)	O4—C4—C3	114.3 (4)
O3—C3—C4	114.9 (4)	C3—O3—C22	116.7 (4)
O4—C4—C5	125.8 (5)	C4—O4—C23	116.4 (4)
C2—C3—O3—C22	−14.6 (9)	C5—C4—O4—C23	−2.3 (8)
C4—C3—O3—C22	166.4 (7)	C3—C4—O4—C23	179.0 (5)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O2*M*$^{\rm i}$	0.92	1.78	2.671 (6)	161.7
O4*M*—H4*M*···O1*M*	0.83	1.64	2.471 (7)	175.6

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

Brucine is a naturally occurring molecule with a well established stereochemistry and no atoms other than C, H, N and O; this enables the structure to be based on a unique set of data with no Friedel equivalents, as anomalous data will make no significant difference to the absolute structure refinement. This also contributes to the low reflection-to-parameter ratio.

Two atoms show rather high displacement parameters, namely, O4*F* in (I) and C22 in (II). Their slight disorder could not be modelled satisfactorily, but it does show clearly, in the case of O4*F*, that there is no stabilizing hydrogen bond, and for C22, that the conformation of methoxy groups is variable, as mentioned above. The site occupancies for O1*W*/O2*W* and O1*W*′ were refined to values near 50%, then fixed for consistency. All H atoms were placed, with the H atoms on O1*W*, O1*W*′ and O2*W* being placed to give an acceptable hydrogen-bonding network, except for H2*WA* which was found in the difference map.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1990*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990*b*); program(s) used to solve structures: *DIRDIF*96 (Beurskens, 1996); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *Cerius*^{2} (Molecular Simulations Inc., 1997) and *SHELXTL* (Sheldrick, 1994) for (I); *Cerius*^{2} (Molecular Simulations Inc., 1997) for (II). For both compounds, software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1243). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1951–1954

Ethyl 3-Hydroxybenzo[*b*]furan-2-carboxylate

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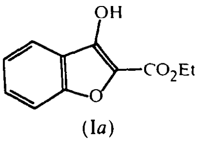
Abstract

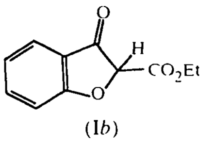
Molecules in the title compound, $C_{11}H_{10}O_4$, occur as centrosymmetric dimers, which lie in parallel planes separated by about 1 Å. Both intra- and intermolecular hydrogen bonding occurs across the –OH···O=C groups of the dimer, in a rhombic arrangement. The non-H atoms are effectively planar in each monomeric unit, with the ethyl groups lying in an extended *trans* configuration. A theoretical study of the equilibrium structures of both the monomeric and dimeric units was made by SCF (self-consistent field) methods with a double-ζ basis set. The monomeric and dimeric structures obtained are very similar to each other, and to the observed structure.

Comment

Ethyl 3-hydroxybenzo[*b*]furan-2-carboxylate, (I), long known as ethyl 3-hydroxycumarilate, is a classical example of a keto–enol tautomeric substance. There is interest in which tautomer, (I*a*) or (I*b*), is present under different conditions; also their reactivity, from the point of view of alternative sites, has been extensively studied in alkaline solution, where both O- and C-alkylation occur (Brandstrom & Forsblad, 1957). We report here the crystal structure of (I).



(I*a*)



(I*b*)

The benzofuran system and the ethoxycarbonyl group in (I) lie in a single plane, with the ethyl group in a staggered conformation. The bond lengths in the heteroaromatic part of the molecule show variable double-bond character, but the bond between C2 and C3 is especially short [1.353 (4) Å], indicative of the enol form of the compound. (I) crystallizes with pairs of molecules disposed about inversion centres connected by intermolecular and intramolecular hydrogen bonds (Fig. 1). The two molecules lie in parallel planes which are separated by 0.986 Å; the bifurcated hydrogen bonds between the OH group and the two carbonyl groups lead to close carbonyl O-atom distances of 2.962 (3) Å. Such a short distance between two formally non-interacting O atoms is unusual, and ascribable to the geometry and strength of the hydrogen-bond system.

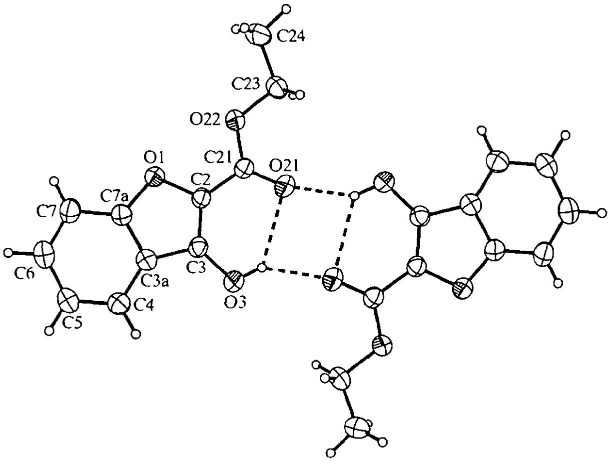


Fig. 1. Inter- and intramolecular hydrogen bonding in (I). Displacement ellipsoids enclose 30% probability surfaces and H atoms are drawn with arbitrary size. The molecules are related by the symmetry operation $2-x$, $2-y$, $-z$.

As a means of probing the structural influence exerted by this hydrogen-bonding system, the monomeric and 'dimeric' structures were optimized at the SCF level using a double-ζ (DZ) basis set. It appears that the monomeric and dimeric structures have comparable bond lengths equal to within 0.001 Å, the only significant difference being the angle C3—O—H, which is 113.7° in the monomer and 116.1° in the dimer. These calculated DZ structures agree with the measured bond lengths to about 1%, except for the distances C21—O21 (2.1%) and C23—C24 (2.5%). Similarly, the difference between the DZ-calculated and observed angles is generally in the range 2–3%, except where hydrogen bonding is involved.

The calculated distances $O21\cdots O21^i$ 3.041 Å [symmetry code: (i) $2-x$, $2-y$, $-z$] and $O3\cdots O21$ 2.822 Å are close to the experimental data. The present level of agreement between theory and experiment is sufficiently good that the present calculated data for the H-atom positions can be presumed reliable; thus, the O3, H3, $H3^i$ and $O3^i$ atoms are close to collinear, the minor deviations from the line being towards the other hydrogen-bonded centres O21 and $O21^i$.

As one would expect from electronegativity differences, all H atoms have positive net Mulliken charges of about +0.22 e (H—C) and +0.53 e (H—O). The neg-

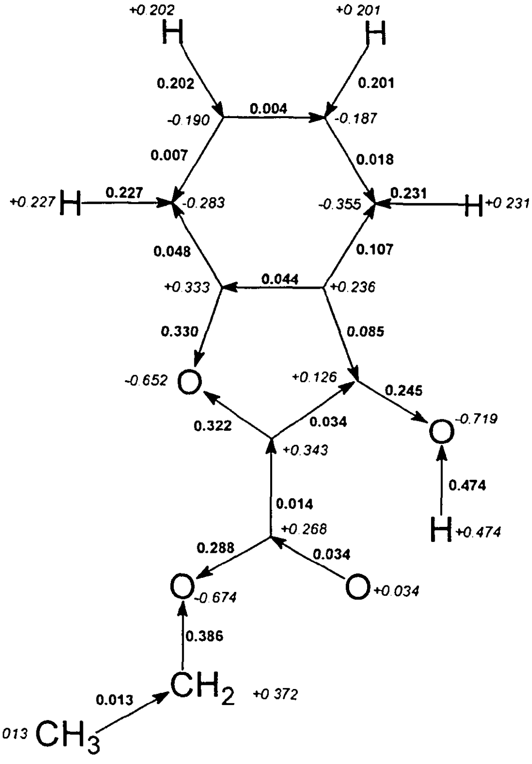


Fig. 2. The σ-electron distribution resolved into a set of bond dipoles. The σ charges are given in italics.

ative charges on the O atoms are variable, with magnitudes O(H) > O(ester) > O(furan). The heterocyclic C atoms are all positive, by very variable amounts (+0.13 to +0.38 e). Ring C—H groups are effectively neutral. Ethyl groups are donors to ether oxygen by 0.37 e, with the carbonyl groups nearly neutral. It is instructive to decompose these overall effects into σ and π components. The derived bond dipoles (Palmer & Findlay, 1974; Palmer & Kennedy, 1976) for the π system show the OH group to be a donor to the ring like the ring O atom, with acceptor centres C2, C3 and C5 in particular. The carbonyl group is strongly polarized towards the O atom, which accepts from both the adjacent C atom and the ether oxygen through the π-electron system. The three singly bonded O atoms are all π donors (+0.11 to +0.18 e) and act as σ acceptors. The doubly bonded O atom is also a π acceptor, but acts as a weak σ donor.

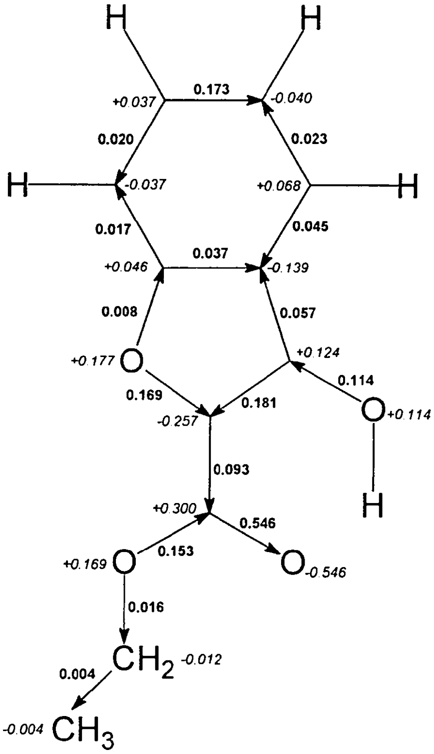


Fig. 3. The π-electron distribution resolved into a set of bond dipoles. The π charges are given in italics.

Experimental

The title compound, (I), was prepared in two stages from ethyl salicylate and ethyl bromoacetate in alkaline conditions, where the initial adduct, the aryloxyacetic ester, was cyclized in the presence of sodium ethoxide to yield the bicyclic compound (I) (Friedlander, 1899; Nepault & Mentzer, 1966). The IR and NMR spectra both showed that the enol form was dominant in solution, in agreement with previous work (Nepault & Mentzer, 1966).

Crystal data

$C_{11}H_{10}O_4$
$M_r = 206.19$
Monoclinic
$P2_1/c$
$a = 8.2441$ (3) Å
$b = 14.5329$ (5) Å
$c = 8.5294$ (3) Å
$\beta = 100.777$ (3)°
$V = 1003.89$ (6) Å^3
$Z = 4$
$D_x = 1.364$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 70 reflections
$\theta = 20$–22°
$\mu = 0.881$ mm^{-1}
$T = 293$ (2) K
Block
0.39 × 0.16 × 0.16 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω–θ scans with ω half-width (1.2 + 0.15tanθ)°
Absorption correction: none
2162 measured reflections
1460 independent reflections
1084 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 59.96°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 16$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.128$
$S = 1.051$
1460 reflections
168 parameters
All parameters refined for some H atoms but only the coordinates refined for others
$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 0.1005P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0024 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Calculated and measured bond lengths (Å)*

	Calculated	Measured
O1—C2	1.397	1.392 (3)
O1—C7a	1.372	1.367 (3)
C2—C3	1.359	1.353 (4)
C3—C3a	1.444	1.430 (4)
C3a—C4	1.398	1.396 (4)
C3a—C7a	1.396	1.389 (4)
C4—C5	1.386	1.369 (4)
C5—C6	1.412	1.396 (5)
C6—C7	1.389	1.368 (5)
C7—C7a	1.388	1.381 (4)
C2—C9	1.443	1.435 (4)
C3—O8	1.346	1.346 (3)
C21—O21	1.239	1.213 (3)
C21—O22	1.329	1.328 (3)
O22—C23	1.466	1.453 (3)
C23—C24	1.518	1.480 (5)
O21—O21$^{\rm i}$	3.041	2.962 (3)
O3—O3$^{\rm i}$	4.979	4 979 (3)
O21—O3	2.822	2.970 (3)
O21—O3$^{\rm i}$	3.014	2.822 (3)

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

Table 2. *Calculated and measured bond angles (°)*

	Calculated	Measured
O1—C2—C3	110.63	110.9 (2)
O1—C2—C21	117.01	120.2 (2)
O1—C7a—C3a	110.59	111.4 (2)
O1—C7a—C7	126.70	125.6 (3)
C2—O1—C7a	106.26	105.4 (2)
C2—C3—C3a	106.86	107.4 (2)
C2—C3—O3	125.45	129.5 (2)
C2—C21—O22	117.01	114.2 (2)
C2—C21—O21	119.40	121.6 (2)
C3—C2—C21	125.64	128.9 (2)
C3—C3a—C7a	105.65	105.0 (2)
C3—C3a—C4	133.86	135.6 (3)
C3a—C3—O3	123.69	123.1 (2)
C3a—C7a—C7	122.74	122.9 (3)
C3a—C4—C5	117.75	118.2 (3)
C4—C3a—C7a	120.49	119.4 (3)
C6—C7—C7a	116.42	116.5 (3)
C4—C5—C6	120.83	121.0 (3)
C5—C6—C7	121.79	121.9 (3)
C21—O22—C23	120.43	117.1 (2)
O22—C21—O21	123.53	124.2 (2)
O22—C23—C24	106.57	107.4 (3)

The equilibrium structures of the monomer and dimer were obtained by *ab initio* Hartree–Fock SCF methods using a double-ζ basis set of Gaussian functions (Huzinaga, 1965; Dunning, 1970). This method is known to give structures close to experiment for small molecules. All calculations were performed with the *GAMESS-UK* suite of programs (Dupuis *et al.*, 1980; Guest *et al.*, 1995). Diffraction data were collected to $2\theta_{\max} = 120°$, the presence of a low-temperature device precluding collection to higher resolution.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL*.

We thank the EPSRC for provision of a four-circle diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1279). Services for accessing these data are described at the back of the journal.

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4′-Methylaminoavarone from *Dysidea avara*†

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(*Received 19 May 1998; accepted 7 July 1998*)

Abstract

The title compound, 2-methylamino-5-[(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthyl)methyl]-2,5-cyclohexadiene-1,4-dione, $C_{22}H_{31}NO_2$, is a natural substance with a sesquiterpenoid-substituted quinone skeleton. As found in all structures of the avarol-avarone family, the quinone ring is almost perpendicular to the bicyclic sesquiterpene system. Some molecular parameters are outside the standard values because of bulky substituents crowding the bicyclic system. The crystal packing is characterized by rows of translated molecules interconnected through hydrogen bonds between the amino groups and O1 carbonyl atoms giving rise to alternate polar layers and van der Waals regions.

Comment

Sponge *Dysidea avara* is a very rich source of secondary metabolites, such as the avarol-avarone pair and derivatives, with sesquiterpenoid-monosubstituted quinone (or hydroquinone) skeletons (Minale *et al.*, 1974; Cimino *et al.*, 1982; De Giulio *et al.*, 1990; Faulkner, 1997). These substances have been widely investigated because of their various biological properties, *e.g.* anti-inflammatory, antileukaemic, antimutagenic, cytotoxic

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† Dedicated to the memory of Professor Luigi Minale.

‡ Associated to the National Institute for the Chemistry of Biological Systems (CNR).

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