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Ethyl (*E*)-3-(2-hydroxyphenyl)-2-(morpholinocarbonyl)propenoate

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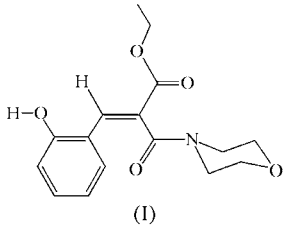
The title compound, $C_{16}H_{19}NO_5$, crystallizes as a centrosymmetric dimer through strong O—H···O hydrogen-bonding interactions between the hydroxyphenyl and morpholinocarbonyl groups. The morpholinocarbonyl group is almost perpendicular to the propenoate moiety. Electron delocalization in the N—C(═O) fragment leads to the formation of hydrogen-bonded *S*(5) ring motifs through C—H···O interactions.

Comment

Lignin-related phenylpropanoids, such as cinnamic acid, are abundant in plant cells and are precursors not only of lignin, the second most abundant carbon compound on earth after cellulose, but also of anthocyanins, phytoalexins and flavonoids (Peng *et al.*, 2003). Many phenylpropanoids are pharmacologically active and thus of pharmaceutical interest (Dixon *et al.*, 1996). The biodegradation of phenylpropanoids is important for the global carbon cycle from an environmental point of view, since these compounds are released from plant wastes as breakdown products from lignin. In view of their importance, augmented further by the potential use of phenylpropanoids as feedstock for bioconversion into valuable molecules (Rosazza *et al.*, 1995), we have analysed the crystal structure of the title compound, (I).



(I)

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The observed bond lengths and angles in

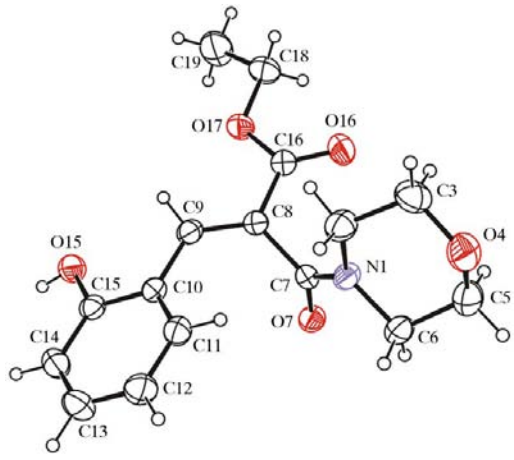


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level.

the hydroxyphenyl group are in agreement with values reported in the literature (Domenicano *et al.*, 1975; Allen *et al.*, 1987). The morpholine ring exhibits a chair conformation, and its bond lengths and angles are comparable to those reported for a related structure (Decken *et al.*, 2003).

The cinnamic acid derivative (I) has a C8═C9 bond length of 1.339 (3) Å, which confirms its double-bond character. The ester and 2-hydroxyphenyl groups are arranged in opposite positions around the double bond [C16—C8═C9—C10 = 177.9 (2)°], giving it an *E* configuration. The ethoxy group points towards the double bond and is almost coplanar with it [C9═C8—C16—O17 = 14.5 (3)°]. These features support the formation of an *S*(5) ring motif (Bernstein *et al.*, 1995) through a soft (Desiraju, 1995) C9(sp^2)—H9···O17 intramolecular hydrogen-bonding interaction [C9···O17 = 2.747 (2) Å], in spite of the small C9—H9···O17 angle (103°). In the same context, the amide moiety is almost coplanar with the neighbouring C6 atom of the morpholine ring [C6—N1—C7—O7 = 2.3 (3)°] and the C6—N1—C7 angle [121.59 (18)°] is slightly less open than the C2—N1—C7 angle [124.81 (18)°]. Another plausible soft *S*(5) hydrogen-bond motif is formed through a C6(sp^3)—H6*A*···O7 interaction [C6···O7 = 2.774 (3) Å and C6—H6*A*···O7 = 103°; Fig. 2]. The hydrogen-bonding geometry is listed in Table 2. This interaction appears as a consequence of the planarity imposed by electron delocalization in the amide N—C(═O) fragment, as indicated by the short N1—C7 distance of only 1.327 (3) Å; this is even shorter than the value found in *N*-benzylmorpholine (1.343 Å; Bennet *et al.*, 1991).

The morpholinocarbonyl group is almost perpendicular to the ester group, with N1—C7—C8—C16 and O7═C7—C8—C16 torsion angles of −81.5 (2) and 97.2 (2)°, respectively. This orthogonal disposition of the two *S*(5) hydrogen-bonding motifs must be dictated by the steric requirements of the morpholine ring, in addition to the restricted rotation of the amide N—C(O) bond (Bennet *et al.*, 1991). The conformation exhibited by (I) in the solid state is similar to that found in solution, as supported by the ^{13}C NMR spectrum, which shows

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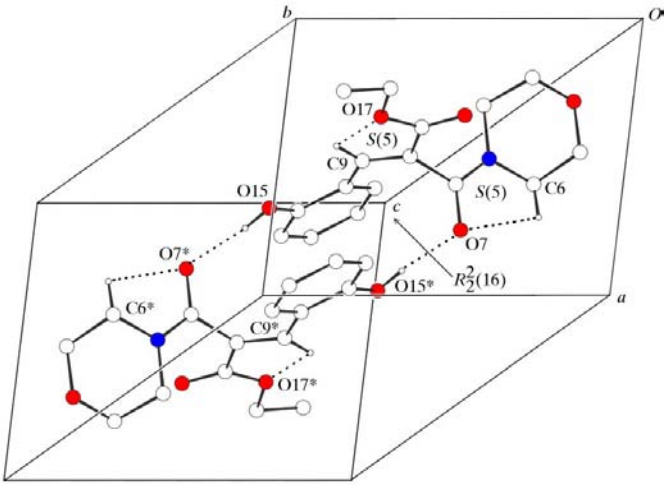

Figure 2
A view of the intra- and intermolecular hydrogen-bonding scheme in the crystal structure of (I). Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

four different signals, at 66.4 and 66.3 p.p.m., and at 46.9 and 41.9 p.p.m., for the CH_2O and CH_2N morpholine ring C atoms, respectively.

Finally, the crystal packing is mediated by a strong (Steiner, 2002) O15—H15···O7^{i} intermolecular interaction [H15···O7^{i} = 1.88 Å, O15···O7^{i} = 2.688 (2) Å and O15—H15···O7^{i} = 168°; symmetry code: (i) $1-x$, $1-y$, $1-z$], leading to dimerization in the *ac* plane. As a result, a 16-membered intermolecular ring is formed, whose topological motif corresponds to the first-level graph-set descriptor $R_2^2(16)$ (Fig. 2). No other hydrogen-bonding interactions linking this centrosymmetric dimer are formed.

Experimental

Compound (I) was synthesized by refluxing equimolar quantities of ethyl coumarin-3-carboxylate (2.12 mmol) and morpholine in dry ethyl alcohol (20 ml) for 24 h. The product crystallized from the reaction mixture as a white solid (56% yield, m.p. 488–493 K). Crystals suitable for X-ray analysis were obtained after slow recrystallization from an ethyl alcohol solution. IR (KBr, cm^{-1}): 1764 (C═O), 1606 (C═C); ^{1}H NMR (p.p.m., DMSO-d_6): 10.3 (*b*, 1H, OH), 7.94 (*s*, 1H, H-vinyl), 7.40 (*d*, 1H, H$_o$), 7.31 (*dd*, 1H, H$_p$), 6.98 (*d*, 1H, H$_m$), 6.80 (*dd*, 1H, H$_m$), 4.22 (*q*, 2H, CH_2), 3.57–3.41 (*m*, 4H, CH_2O), 3.22–3.11 (*m*, 4H, CH_2N), 1.24 (*t*, 3H, CH_3); ^{13}C NMR (p.p.m., DMSO-d_6): 165.5 (COO), 164.9 (NCO), 157.4 (C-OH), 135.2 (C-Ar), 132.9 (C$_p$), 128.9 (C$_o$), 126.1 (C$_i$), 120.3 (CCO), 120.0 and 116.6 (C$_m$), 66.4 and 66.3 (CH_2O), 46.9 and 41.9 (CH_2N), 16.6 (CH_2), 14.8 (CH_3).

Crystal data

$C_{16}H_{19}NO_5$
M_r = 305.32
Triclinic, $P\overline{1}$
a = 7.790 (2) Å
b = 9.971 (2) Å
c = 10.832 (2) Å
α = 72.59 (3)°
β = 74.79 (3)°
γ = 75.64 (3)°
V = 761.5 (3) Å^3
Z = 2
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 600 reflections
θ = 20–25°
μ = 0.10 mm^{-1}
T = 293 (2) K
Block, colourless
0.40 × 0.30 × 0.30 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
5151 measured reflections
3003 independent reflections
1669 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 26.1°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.104
S = 1.01
3003 reflections
200 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$ where $P = (F_o^2 + 2F_o^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.027 (3)

Table 1
Selected geometric parameters (Å, °).

O4—C3	1.416 (3)	O17—C18	1.446 (3)
O4—C5	1.419 (3)	N1—C2	1.464 (3)
O7—C7	1.240 (3)	N1—C7	1.327 (3)
O15—C15	1.357 (3)	N1—C6	1.463 (3)
O16—C16	1.205 (3)	C8—C9	1.339 (3)
O17—C16	1.324 (3)		
C3—O4—C5	110.11 (19)	N1—C7—C8	119.2 (2)
C16—O17—C18	116.27 (18)	O7—C7—N1	122.86 (19)
C2—N1—C7	124.81 (18)	O16—C16—O17	123.54 (19)
C6—N1—C7	121.59 (18)	O17—C16—C8	113.81 (17)
C2—N1—C6	113.39 (17)	O16—C16—C8	122.63 (19)
O7—C7—C8	117.9 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O15—H15···O7^{i}	0.82	1.88	2.688 (2)	168
C6—H6A···O7	0.97	2.39	2.774 (3)	103
C9—H9···O17	0.93	2.38	2.747 (2)	103

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

All H atoms were positioned geometrically and included in the refinement as riding atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97 and *WinGX*2003 (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1065). Services for accessing these data are described at the back of the journal.

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