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Ethyl 2-*trans*-cinnamoylacetoacetate

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Low-temperature X-ray diffraction data show that ethyl 2-acetyl-3-oxo-5-phenylpent-4-enoate ($C_{15}H_{16}O_4$) exists in the same single enol tautomer in the crystal phase as indicated by spectroscopic data for the compound in solution. The adopted conformation is that with the longest possible conjugation combined with the enol H atom being bonded to the O atom closest to the most electronegative substituent in the planar cinnamoyl acetate unit. Weak hydrogen bonds of the type $C—H\cdots O$ are suggested.

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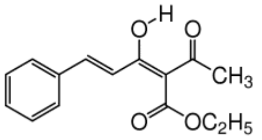
Key indicators

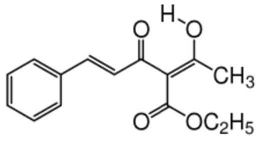
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.079
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The reaction of the boron complex of 2-*trans*-cinnamoyl acetic ethyl ester (CAA) with aromatic or heteroaromatic aldehydes and subsequent acid hydrolysis opened a new procedure for the synthesis of deep coloured β,β'-tricarbonyl compounds


(1a)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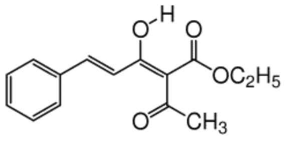
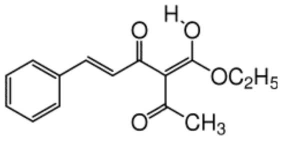

(2a)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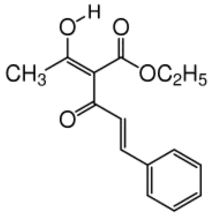
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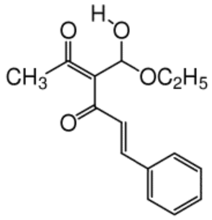
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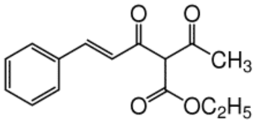
(4rs)

DOI: 10.1107/S1600536801010583

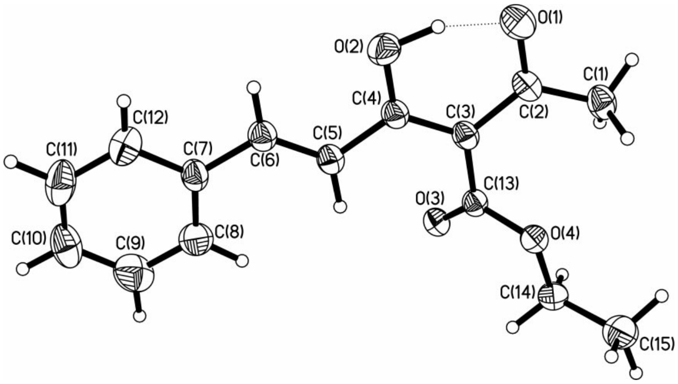

Figure 1
Drawing of the CAA molecule showing the numbering of the atoms and the displacement ellipsoids at a 50% probability level.

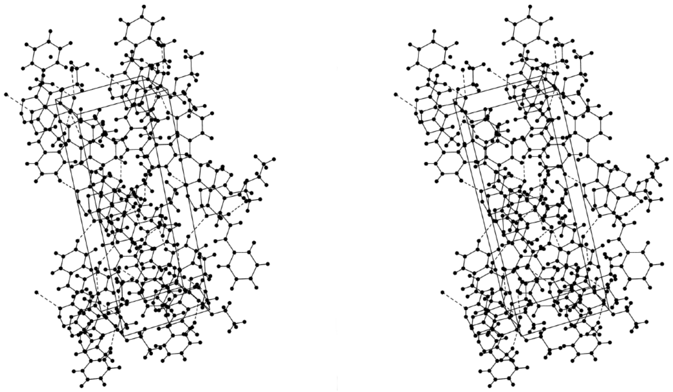

Figure 2
Stereographic illustration of the molecular packing of CAA molecules in the crystals.

(Arrieta, 1993). This was an extension of the Pabon reaction (Pabon, 1964) for β-diketo esters and showed the ability and reactivity of the acetyl group for further condensation reactions. The β,β'-tricarbonyl compounds are interesting molecules also because of the possibility of adopting several different enol tautomer conformations. Thus, the title compound, (4rs), may exist in seven different forms.

Earlier IR spectroscopic studies of the title compound (Arrieta *et al.*, 1988) have shown that the carboethoxy group is peripheral and non-coordinating in copper complexes. Moreover, a recent ^{13}C NMR study (Emelina *et al.*, 1999) has indicated that the CAA molecule adopts the (1a) conformation in solution. The postulated chelate bond between the acetyl group and the cinnamoyl group in CAA has been reinvestigated in the solid solution (KBr) and in liquid solution ($CHCl_3$) using IR and NMR spectroscopy. The IR region at 1310 cm^{-1} in CCl_4 was assigned by Forsen (Forsen & Nilson, 1959) to the cinnamoyl group, and probably refers to the group C(=O)CH=CH. The ^{13}C NMR spectrum in the same solvent confirms, in accord with recent studies (Emelina *et al.*, 1999), the absence of any tautomers other than (1a). The ^{1}H NMR spectrum in $CDCl_3$ shows only one signal for the enol proton (17.60 p.p.m.) in contrast to 2-acetylbenzoylacetates where at least two are found (Sicker & Mann, 1988). The reason for this seems unclear and NMR studies of such compounds are in progress (Arrieta & Radeglia, 2001). The structural study of 3-benzoyl-6-phenyl-hex-5-ene-2,4-dione (Arrieta *et al.*, 1995), which differs from the title compound only in the exchange of the benzoyl group with a carbethoxy group, showed that the conformation adopted in the crystal phase is that where the longest possible conjugation in the molecule, as well as the positioning of the enol H atom at the oxygen closest to the most electronegative substituent, are simultaneously satisfied. The result of the present investigation shows that the 6-phenylhex-5-ene-2,4-dione parts of the two molecules have virtually identical measures in bond lengths, angles and conformation. This supports the idea that the conjugation and the electronegativities of the enol ring substituents are determining factors for the conformation and the position of the enol H atom. It may be seen from the Scheme, that only conformation (1a) fulfils the two criteria. In the crystal structure of CAA, the molecules related by rotation axes are stacked along the *b* axis with overlapping enol and carboxylate groups. The distances between the planes through these two groups are 3.423 (2) and 3.391 (2) Å, respectively. The closest contacts between molecules occur through C—H···O interactions. The geometry of these interactions (Table 2) and the fact that such interactions are repeatedly found in the crystal structures of this group of molecules (Mostad, 1994; Arrieta *et al.*, 1995, 2000), indicate that they may be considered as examples of weak hydrogen bonds (Desiraju & Steiner, 1999). A drawing of the molecule with the numbering of the atoms and their vibrational ellipsoids is given in Fig. 1. The packing of the molecules is displayed in Fig. 2.

Experimental

The title compound was synthesized according to a known procedure (Arrieta, 1993). The crystals grown by cooling a saturated warm solution in toluene have a melting point of 318 K. The IR spectra were obtained from a Nicolet 205 FT–IR spectrometer using the KBr pellet technique as well as liquid solution (0.4656 *M*, δ = 2.2 mm) The NMR spectra (^{1}H and ^{13}C) were recorded on Bruker instruments AC 250 and ARX 300. The signals δ = 7.26 p.p.m. ^{1}H and δ = 77.7 p.p.m. ^{13}C for $CDCl_3$ were selected as internal standards. Two characteristic IR absorption bands at 1698 and 1624 cm^{-1} with about equal intensities (in KBr) were assigned to the non coordinated carbethoxy group and the cinnamoyl group, in coordination with the acyl group, respectively. In chloroform solution (0.47 *M*), the first band is shifted to 1701 cm^{-1} (ε = 39 l mol^{-1} cm^{-1} and the chelate band to 1630 cm^{-1} (ε = 44 l mol^{-1} cm^{-1}. In KBr and $CHCl_3$, a similar profile was found for the bands at 1268 and 1308 cm^{-1} (KBr) and 1278 and 1308 cm^{-1} ($CHCl_3$).

Crystal data

$C_{15}H_{16}O_4$
M_r = 260.28
Orthorhombic, *Pnn*2
a = 21.698 (4) Å
b = 7.3390 (15) Å
c = 8.6380 (17) Å
V = 1375.5 (5) Å^3
Z = 4
D_x = 1.257 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 1024 reflections
θ = 3.7–26.3°
μ = 0.09 mm^{-1}
T = 123 (2) K
Needle, yellow
0.4 × 0.3 × 0.3 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.964$, $T_{\max} = 0.973$
13 464 measured reflections
2813 independent reflections
2703 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 26.4°$
$h = -27 \rightarrow 26$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.06$
2813 reflections
236 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.275P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C4—O2	1.3081 (18)	C3—C13	1.4882 (18)
C4—C3	1.4066 (19)	C6—C5	1.3398 (19)
C4—C5	1.4601 (18)	C6—C7	1.466 (2)
O1—C2	1.2643 (18)	O4—C13	1.3390 (16)
O1—H2	1.45 (3)	O4—C14	1.4594 (18)
O2—H2	1.03 (3)	O3—C13	1.2091 (17)
C2—C3	1.4481 (19)	C14—C15	1.505 (2)
C2—C1	1.498 (2)		
O2—C4—C3	120.67 (13)	C2—C3—C13	120.94 (12)
O2—C4—C5	116.06 (12)	C5—C6—C7	126.44 (14)
C3—C4—C5	123.25 (14)	C6—C5—C4	121.24 (13)
C2—O1—H2	101.0 (11)	C8—C7—C6	122.41 (14)
C4—O2—H2	103.2 (15)	C12—C7—C6	119.42 (14)
O1—C2—C3	119.92 (14)	C13—O4—C14	116.54 (11)
O1—C2—C1	117.34 (13)	O4—C14—C15	106.98 (13)
C3—C2—C1	122.68 (14)	O3—C13—O4	123.01 (13)
C4—C3—C2	118.30 (14)	O3—C13—C3	125.16 (13)
C4—C3—C13	120.71 (12)	O4—C13—C3	111.83 (11)
C4—C3—C13—O3	42.0 (2)	C4—C3—C13—O4	−137.70 (12)
C2—C3—C13—O3	−135.22 (14)	C2—C3—C13—O4	45.06 (17)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	1.03 (3)	1.45 (3)	2.427 (2)	157 (2)
C10—H10···O2$^{\rm i}$	0.98 (2)	2.79 (2)	3.707 (2)	155 (2)
C11—H11···O3$^{\rm ii}$	0.97 (2)	2.52 (2)	3.349 (2)	143 (2)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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