Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The polyfunctionalized enaminone ethyl [(*Z*)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl-idenemethyl)-1-methyl-3-oxo-but-1-enylamino]-acetate

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Received 16 November 2004
Accepted 19 November 2004
Online 27 November 2004

The solid-state structure of the title enaminone, $C_{15}H_{17}N_1O_7$, the C adduct obtained from the reaction of 4-aminopent-3-en-2-one with methoxymethylene Meldrum's acid, has been investigated by X-ray diffraction, and several structural features are different from the previously described structure of the corresponding N adduct. The carbonyl group of the enaminone moiety of the C adduct is not coplanar with the enamine fragment. One bifurcated intramolecular N—H$\cdots$O hydrogen bond [2.688 (2) and 2.668 (2) Å] and two intermolecular C—H$\cdots$O hydrogen bonds [3.339 (3) and 3.379 (3) Å] are observed. The structure packs in a linear fashion along the [100] direction.

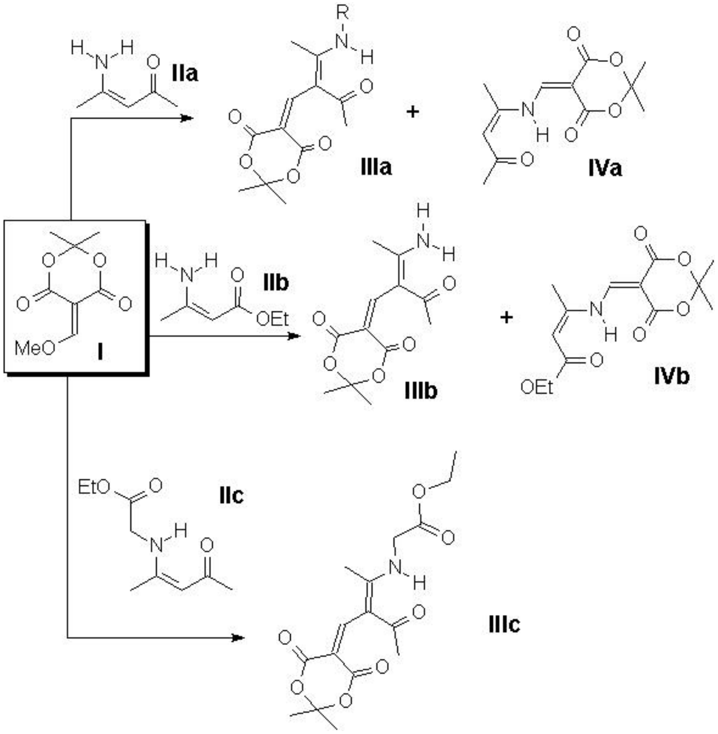
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.056
wR factor = 0.162
Data-to-parameter ratio = 12.9

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

Comment

The chemistry of enaminones and their derivatives has attracted the attention of numerous researchers because of the ambiphilic and ambidentate properties of these compounds and their potential in the synthesis of heterocyclic compounds (Negri *et al.*, 2004; Lue & Greenhill, 1997; Kuckländer, 1994). Because of these applications, several protocols for the synthesis of functionalized enaminones have been developed (Ferraz & Pereira, 2004).



Recently we described the reaction of methoxymethylene Meldrum's acid, (I), with acyclic enaminones (Cunha *et al.*,

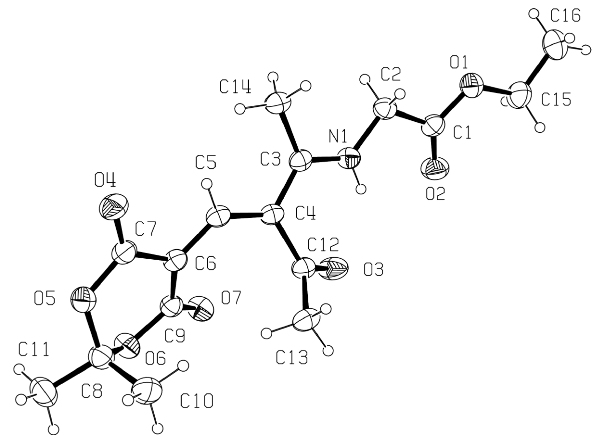


Figure 1
The molecular structure of (III*c*), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The disordered H atoms of the C13 atom are not shown for clarity.

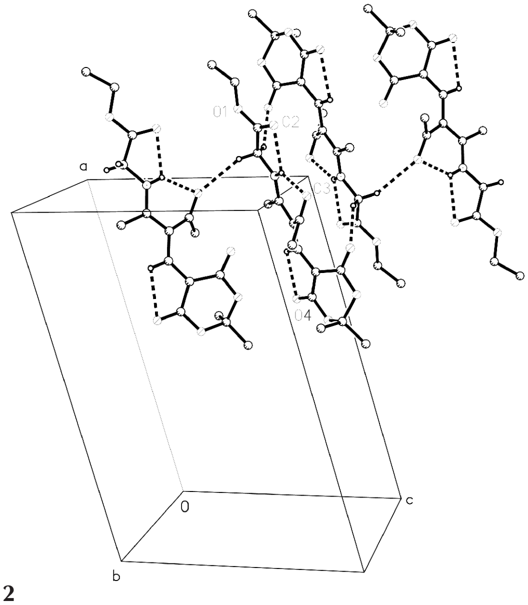


Figure 2
Part of the packing. Intra- and intermolecular hydrogen bonds are shown as dashed lines. Only the H atoms involved in hydrogen bonds are shown.

2003). Because enaminones may act as an ambident nucleophile by reaction at the N atom and at the β-carbon, the reactions of enaminones and methoxymethylene Meldrum's acid depend on the *N*-amine substituent, according to the scheme.

C adducts, (III*a*)–(III*c*), are obtained with an NHR substituent (*R* = alkyl) and N adducts, (IV*a*)–(IV*b*), with the NH_2 group. While an X-ray study of two N adducts (IV*a*)–(IV*b*) was described by Cunha *et al.* (2003), no structural description of the C adduct of acyclic enaminones and (I) has been reported.

An *ORTEP* (Farrugia, 1997) plot of (III*c*) is shown in Fig. 1. Selected bond distances, angles and torsion angles are given in Table 1. The Meldrum's acid group has a distorted boat conformation, indicated by the Cremer & Pople (1975) parameters O5$\rightarrow$C7$\rightarrow \ldots \rightarrow$C8 [$Q$ = 0.450 (2) Å, θ = 68.8 (3)° and φ = 293.1 (3)°]. The enaminone moiety of the C adduct is not completely coplanar, unlike the structures of N adducts (IV*a*) and (IV*b*) (Cunha *et al.*, 2003). The corresponding carbonyl C12═O3 group in these N adducts is completely coplanar with atoms C4, C3 and N1, while the C12═O3 carbonyl group in C adduct (III*c*) is out of the plane formed by atoms N1, C3 and C4, as can be seen from the C3—C4—C12—O3 torsion angle of −39.0 (3)°. This should be attributed to conjugation involving the C5/C6/C7/O4 fragment of the Meldrum's acid of the C adduct and atoms C4, C3 and N1 of the enaminone moiety, which afford a better electron delocalization than the conjugation involving atoms C4, C3, N1 and C12═O3. Additionally, the C6—C5—C4 angle of 130.6 (2)° is somewhat large and reflects the steric repulsion of the disordered H atoms of methyl atom C13 and the carbonyl atom O7 of the six-membered ring.

The molecular packing of (III*c*) is stabilized through a hydrogen-bonded network, as shown in Fig. 2, with the geometric parameters in Table 2. There is one bifurcated intramolecular hydrogen bond between atoms O2 and O3 and the NH group, N1—H1N$\cdots$O2 [2.688 (2) Å] and N1—H1N$\cdots$O3 [2.668 (2) Å], providing two flattened rings. In addition, another intramolecular hydrogen bond, C5—H5$\cdots$O4 [2.814 (3) Å], stabilizes the molecule. The intermolecular hydrogen bond C2—H2*A*$\cdots$O7$^{\rm i}$ [3.339 (3) Å; symmetry code: (i) $2 - x, -y, 2 - z$] links two neighbouring molecules in a centrosymmetric dimeric form. The hydrogen bond C2—H2*B*$\cdots$O3$^{\rm ii}$ [3.379 (3) Å; symmetry code: (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$] completes the packing, with the molecules stacked in molecular columns parallel to the [100] direction.

Experimental

Compound (III*c*) was prepared as described by Cunha *et al.* (2003). A solution of Meldrum's acid (2 mmol) in trimethyl orthoformate (2 ml) was heated at reflux for 2 h, after which time the solvent was evaporated. The solid that formed was dissolved in CH_2Cl_2 (5 ml), enaminone (II*c*) (2 mmol) was added and the solution was allowed to stand at room temperature for 24 h. The solvent was evaporated and the crude residue was recrystallized from CH_2Cl_2/petroleum ether, affording (III*c*) as a yellow solid (yield 67%; m.p. 412–415 K). IR (KBr): 3223, 1736, 1690, 1647, 1442 cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.34 (3H, *t*, J = 7.1 Hz), 1.74 (6H, *s*), 2.22 (3H, *s*), 4.26 (2H, *d*, J = 5.1 Hz), 4.32 (2H, *q*, J = 7.1 Hz), 8.72 (1H, *s*), 12.64 (1H, *br s*). ^{13}C NMR ($CDCl_3$): 14.1 (CH_3), 18.6 (CH_3), 27.4 (CH_3), 27.7 (CH_3), 46.1 (CH_2), 62.7 (CH_2), 99.3 (C), 103.3 (C), 111.2 (C), 154.9 (CH), 162.3 (C), 164.5 (C), 166.6 (C), 173.5 (C), 197.5 (C). MS *m*/*z* (%): 339 [M^+, 34%], 281 (62%), 237 (56%), 135 (100%). Analysis calculated for $C_{16}H_{21}NO_7$: C 56.64, H 6.19, N 4.13%; found: C 56.47, H 6.09, N 4.04%. Single crystals were obtained by diffusion of petroleum ether into a solution of (III*c*) in CH_3Cl at room temperature.

Crystal data

$C_{16}H_{21}NO_7$
M_r = 339.34
Monoclinic, $P2_1/c$
a = 16.324 (2) Å
b = 9.478 (1) Å
c = 11.062 (2) Å
β = 103.69 (1)°
V = 1662.9 (4) Å^3
Z = 4
D_x = 1.355 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.1–28.7°
μ = 0.90 mm^{-1}
T = 293 (2) K
Prism, yellow
0.33 × 0.18 × 0.15 mm

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Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3072 measured reflections
2978 independent reflections
2304 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$

$\theta_{\rm max} = 67.2°$
$h = 0 \rightarrow 19$
$k = -11 \rightarrow 0$
$l = -13 \rightarrow 12$
2 standard reflections
frequency: 129 min
intensity decay: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.163$
$S = 1.07$
2978 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1046P)^2 + 0.187P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.010 (1)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.322 (3)	O5—C8	1.441 (3)
O1—C15	1.453 (3)	O6—C9	1.363 (2)
O2—C1	1.196 (3)	O6—C8	1.428 (3)
O3—C12	1.226 (2)	O7—C9	1.210 (2)
O4—C7	1.205 (3)	N1—C3	1.326 (3)
O5—C7	1.364 (3)	N1—C2	1.445 (3)
C1—O1—C15	117.58 (18)	C6—C5—C4	130.56 (19)
C3—C4—C12—O3	−39.0 (3)	C5—C4—C12—C13	−37.6 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O2	0.85 (3)	2.29 (3)	2.688 (2)	109 (3)
N1—H1N···O3	0.85 (3)	1.99 (3)	2.668 (2)	135 (3)
C5—H5···O4	0.96 (3)	2.34 (3)	2.814 (3)	110 (2)
C2—H2*A*···O7$^{\rm i}$	0.95 (4)	2.50 (3)	3.339 (3)	147 (3)
C2—H2*B*···O3$^{\rm ii}$	0.93 (3)	2.51 (3)	3.379 (3)	155 (3)

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

H atoms bonded to atoms N1, C5 and C2 were found in difference Fourier maps and were refined with $U_{\rm iso}({\rm H}) = 0.105$ Å^2. All other H atoms were placed in calculated positions (C—H = 0.96 and 0.97 Å) and treated as riding atoms [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm C}_{\rm methyl})$]; those of methyl atom C13 were refined as disordered (occupancies = 0.50).

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1993); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico–CNPq (Edital Universal-2002, Processo 474592/03-0), Fundação de Apoio à Pesquisa–FUNAPE/UFG. We also thank the Brazilian Agencies for fellowships to JF (CAPES) and IV (CNPq).

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