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(*Z*)-Ethyl 3-(2,4,6-trimethylanilino)but-2-enoate

Manuel Amézquita-Valencia,* Simón Hernández-Ortega,* G. Alejandra Suárez-Ortiz, Rubén Alfredo Toscano and Armando Cabrera

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México 04510, Mexico
Correspondence e-mail: majo00@yahoo.com, simonho@unam.mx

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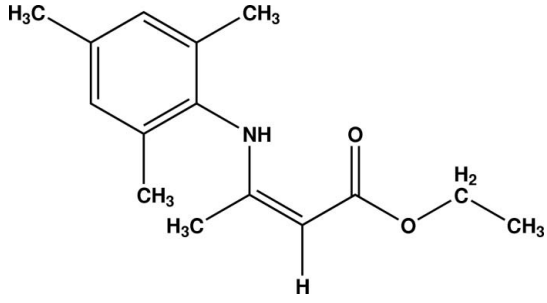
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.049; wR factor = 0.145; data-to-parameter ratio = 15.9.

The title compound, $C_{15}H_{21}NO_2$, was obtained by the reaction of acetoacetate with 2,4,6-trimethylaniline using Mexican bentonitic clay as a catalyst. It crystallizes in the enamine form. The β-enamino ester residue is almost perpendicular to the aromatic ring [dihedral angle = 88.10 (6)°]. The molecular conformation is stabilized by a strong intramolecular N—H···O hydrogen bond. In addition, the N—H group forms a weak intermolecular N—H···O hydrogen bond linking the molecules into centrosymmetric dimers.

Related literature

For enamino esters as intermediates in the synthesis of natural products, see: Marchand *et al.* (1994). β-Enamino esters are useful in synthesis of pharmaceuticals and bioactive heterocycles (Spivey *et al.*, 2003) and as precursors for the preparation of antibacterial, anticonvulsant (Michael *et al.*, 2001), anti-inflamatory and antitumour agents. For the functionalization of these compounds by the introduction of different substituents on the nitrogen, α-carbon and β-carbonylic carbon atoms, see: Braibante *et al.* (2002).



Experimental

Crystal data

$C_{15}H_{21}NO_2$
M_r = 247.33
Monoclinic, $P2_1/c$
a = 8.5647 (8) Å
b = 20.6131 (19) Å
c = 8.2404 (8) Å
β = 93.976 (2)°
V = 1451.3 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 298 K
0.48 × 0.37 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.970, T_{max} = 0.989
11717 measured reflections
2634 independent reflections
2160 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.145
S = 1.05
2634 reflections
166 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.82 (2)	2.08 (2)	2.7516 (18)	138.7 (17)
N1—H1···O1^{i}	0.82 (2)	2.60 (2)	3.2201 (18)	133.1 (16)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5072).

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supporting information

Acta Cryst. (2009). E**65**, o2728 [https://doi.org/10.1107/S160053680903949X]

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S1. Comment

The enamino esters are gaining increased interest, which are known as important intermediates for the synthesis of natural products (Marchand *et al*, 1994). The *β*-enamino esters are useful in synthesis of pharmaceuticals and bioactive heterocycles (Spivey *et al.*, 2003) and as precursors for the preparation of antibacterial, anticonvulsant (Michael *et al.*, 2001), anti-inflamatory and antitumour agents. The functionalization of these compounds by the introduction of different substituents on the nitrogen atom, the *α*-carbon and *β*-carbonylic carbon atoms has been studied (Braibante *et al.*, 2002).

The molecular structure and the atomic numbering scheme is shown in Fig. 1. The trimethylyphenyl substituent is almost perpendicular to the *β*-enaminoester function forming a dihedral angle of 88.10 (6)°.

S2. Experimental

A mixture of ethyl acetoacetate (5 mmol), 2,4,6-trimethylaniline (5 mmol) were dispersed on Actisil-FF (1 g, Mexican Bentonitic Clay) and the mixture was stirred at r.t overnight. The product was extracted by washing the clay with CH_2Cl_2 (3x10mL), dried (Na_2SO_4), filtred and the solvent was removed *in vacuo*. The crude product was purified by column chromatography and recrystallized from hexane. Yield: 92%, *M.p. 65.4°C*

S3. Refinement

H atom on amine group was found in Fourier map and its coordinates were refined with U_{iso}(H) = 1.2 U_{eq}(N). H atoms bonded to C atoms were placed in geometrically idealized positions [C-H = 0.97 Å (for CH_2) and 0.96 Å (for CH_3)] and refined using a riding model with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}C(methyl).

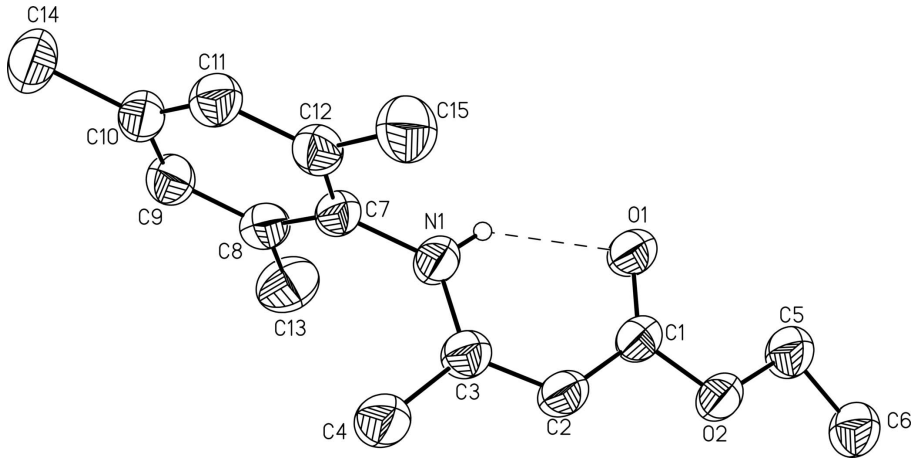

Figure 1

The Molecular structure with the atom numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms bonded to C omitted. The intramolecular hydrogen bond is shown as a dashed line.

(*Z*)-Ethyl 3-(2,4,6-trimethylanilino)but-2-enoate

Crystal data

$C_{15}H_{21}NO_2$
$M_r = 247.33$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.5647\ (8)$ Å
$b = 20.6131\ (19)$ Å
$c = 8.2404\ (8)$ Å
$\beta = 93.976\ (2)°$
$V = 1451.3\ (2)$ Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.132$ Mg m^{-3}
Melting point: 338.2 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5426 reflections
$\theta = 2.6–25.3°$
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Plates, colorless
0.48 × 0.37 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.661 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.970$, $T_{max} = 0.989$
11717 measured reflections
2634 independent reflections
2160 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.0°$
$h = -10\rightarrow10$
$k = -24\rightarrow24$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.145$
$S = 1.05$
2634 reflections
166 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 0.188P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.34094 (14)	0.02629 (6)	0.57044 (15)	0.0678 (4)
O2	0.12297 (13)	0.06508 (5)	0.67115 (14)	0.0634 (3)
N1	0.48468 (17)	0.11091 (7)	0.36990 (19)	0.0608 (4)
H1	0.475 (2)	0.0741 (10)	0.407 (2)	0.073*
C1	0.25234 (18)	0.07166 (8)	0.58833 (18)	0.0531 (4)
C2	0.26799 (18)	0.13592 (8)	0.5250 (2)	0.0572 (4)
H2	0.1988	0.1676	0.5560	0.069*
C3	0.37828 (18)	0.15303 (8)	0.4223 (2)	0.0559 (4)
C4	0.3850 (2)	0.22125 (9)	0.3585 (3)	0.0767 (6)
H4A	0.4923	0.2344	0.3555	0.115*
H4B	0.3321	0.2499	0.4285	0.115*
H4C	0.3349	0.2230	0.2507	0.115*
C5	0.0901 (2)	0.00058 (9)	0.7287 (3)	0.0746 (5)
H5A	0.1642	−0.0108	0.8185	0.089*
H5B	0.0998	−0.0307	0.6421	0.089*
C6	−0.0711 (2)	−0.00040 (10)	0.7828 (2)	0.0733 (5)
H6A	−0.0964	−0.0435	0.8164	0.110*
H6B	−0.1433	0.0128	0.6946	0.110*
H6C	−0.0782	0.0289	0.8725	0.110*
C7	0.60799 (18)	0.12825 (7)	0.27088 (19)	0.0520 (4)
C8	0.58802 (19)	0.12037 (8)	0.1023 (2)	0.0568 (4)
C9	0.7112 (2)	0.13715 (8)	0.0097 (2)	0.0603 (4)
H9	0.6984	0.1328	−0.1027	0.072*
C10	0.85176 (19)	0.16000 (8)	0.0787 (2)	0.0568 (4)
C11	0.86788 (19)	0.16666 (8)	0.2457 (2)	0.0577 (4)
H11	0.9623	0.1819	0.2938	0.069*
C12	0.74836 (19)	0.15143 (7)	0.34424 (19)	0.0549 (4)
C13	0.4379 (2)	0.09401 (11)	0.0225 (3)	0.0857 (6)
H13A	0.4511	0.0857	−0.0903	0.129*
H13B	0.3556	0.1251	0.0319	0.129*
H13C	0.4112	0.0544	0.0752	0.129*
C14	0.9846 (2)	0.17663 (10)	−0.0250 (3)	0.0794 (6)

H14A	1.0610	0.2021	0.0375	0.119*
H14B	0.9449	0.2010	−0.1182	0.119*
H14C	1.0322	0.1374	−0.0603	0.119*
C15	0.7719 (3)	0.15816 (11)	0.5262 (2)	0.0779 (6)
H15A	0.8812	0.1640	0.5567	0.117*
H15B	0.7350	0.1197	0.5771	0.117*
H15C	0.7146	0.1951	0.5608	0.117*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0634 (7)	0.0594 (7)	0.0838 (8)	0.0124 (6)	0.0279 (6)	0.0107 (6)
O2	0.0624 (7)	0.0567 (7)	0.0746 (7)	0.0074 (5)	0.0297 (6)	0.0078 (5)
N1	0.0599 (8)	0.0490 (8)	0.0766 (9)	0.0057 (6)	0.0279 (7)	0.0094 (6)
C1	0.0497 (8)	0.0573 (9)	0.0535 (8)	0.0036 (7)	0.0120 (7)	−0.0022 (6)
C2	0.0530 (9)	0.0534 (9)	0.0672 (10)	0.0071 (7)	0.0176 (7)	−0.0019 (7)
C3	0.0543 (9)	0.0506 (8)	0.0639 (9)	0.0035 (7)	0.0119 (7)	0.0002 (7)
C4	0.0776 (12)	0.0550 (10)	0.1014 (14)	0.0119 (9)	0.0333 (11)	0.0115 (9)
C5	0.0786 (12)	0.0627 (11)	0.0861 (12)	0.0072 (9)	0.0319 (10)	0.0177 (9)
C6	0.0698 (12)	0.0707 (11)	0.0814 (12)	−0.0063 (9)	0.0192 (9)	0.0079 (9)
C7	0.0514 (9)	0.0451 (8)	0.0610 (9)	0.0051 (6)	0.0156 (7)	0.0047 (6)
C8	0.0527 (9)	0.0570 (9)	0.0610 (9)	0.0046 (7)	0.0056 (7)	−0.0013 (7)
C9	0.0667 (10)	0.0639 (10)	0.0510 (8)	0.0071 (8)	0.0102 (7)	0.0015 (7)
C10	0.0594 (10)	0.0492 (8)	0.0636 (9)	0.0036 (7)	0.0186 (7)	0.0058 (7)
C11	0.0534 (9)	0.0518 (9)	0.0683 (10)	−0.0035 (7)	0.0079 (7)	0.0008 (7)
C12	0.0610 (10)	0.0492 (8)	0.0552 (9)	0.0056 (7)	0.0081 (7)	0.0026 (6)
C13	0.0639 (12)	0.1009 (16)	0.0914 (14)	−0.0044 (10)	−0.0012 (10)	−0.0153 (12)
C14	0.0781 (13)	0.0738 (12)	0.0907 (14)	−0.0036 (10)	0.0375 (11)	0.0090 (10)
C15	0.0872 (14)	0.0882 (14)	0.0583 (10)	0.0039 (11)	0.0061 (9)	−0.0009 (9)

Geometric parameters (Å, º)

O1—C1	1.2196 (18)	C7—C8	1.397 (2)
O2—C1	1.3479 (18)	C8—C9	1.388 (2)
O2—C5	1.446 (2)	C8—C13	1.505 (3)
N1—C3	1.351 (2)	C9—C10	1.378 (2)
N1—C7	1.4243 (19)	C9—H9	0.9300
N1—H1	0.82 (2)	C10—C11	1.380 (2)
C1—C2	1.433 (2)	C10—C14	1.509 (2)
C2—C3	1.358 (2)	C11—C12	1.386 (2)
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.504 (2)	C12—C15	1.506 (2)
C4—H4A	0.9600	C13—H13A	0.9600
C4—H4B	0.9600	C13—H13B	0.9600
C4—H4C	0.9600	C13—H13C	0.9600
C5—C6	1.481 (3)	C14—H14A	0.9600
C5—H5A	0.9700	C14—H14B	0.9600
C5—H5B	0.9700	C14—H14C	0.9600

C6—H6A	0.9600	C15—H15A	0.9600
C6—H6B	0.9600	C15—H15B	0.9600
C6—H6C	0.9600	C15—H15C	0.9600
C7—C12	1.392 (2)		

C1—O2—C5	116.36 (12)	C9—C8—C7	118.18 (15)
C3—N1—C7	124.42 (14)	C9—C8—C13	120.59 (16)
C3—N1—H1	112.7 (13)	C7—C8—C13	121.23 (16)
C7—N1—H1	122.8 (13)	C10—C9—C8	122.28 (15)
O1—C1—O2	121.62 (14)	C10—C9—H9	118.9
O1—C1—C2	126.15 (14)	C8—C9—H9	118.9
O2—C1—C2	112.22 (13)	C9—C10—C11	117.98 (15)
C3—C2—C1	123.61 (14)	C9—C10—C14	121.04 (16)
C3—C2—H2	118.2	C11—C10—C14	120.98 (17)
C1—C2—H2	118.2	C10—C11—C12	122.32 (15)
N1—C3—C2	123.10 (15)	C10—C11—H11	118.8
N1—C3—C4	116.49 (15)	C12—C11—H11	118.8
C2—C3—C4	120.40 (14)	C11—C12—C7	118.29 (15)
C3—C4—H4A	109.5	C11—C12—C15	120.61 (16)
C3—C4—H4B	109.5	C7—C12—C15	121.08 (15)
H4A—C4—H4B	109.5	C8—C13—H13A	109.5
C3—C4—H4C	109.5	C8—C13—H13B	109.5
H4A—C4—H4C	109.5	H13A—C13—H13B	109.5
H4B—C4—H4C	109.5	C8—C13—H13C	109.5
O2—C5—C6	108.55 (15)	H13A—C13—H13C	109.5
O2—C5—H5A	110.0	H13B—C13—H13C	109.5
C6—C5—H5A	110.0	C10—C14—H14A	109.5
O2—C5—H5B	110.0	C10—C14—H14B	109.5
C6—C5—H5B	110.0	H14A—C14—H14B	109.5
H5A—C5—H5B	108.4	C10—C14—H14C	109.5
C5—C6—H6A	109.5	H14A—C14—H14C	109.5
C5—C6—H6B	109.5	H14B—C14—H14C	109.5
H6A—C6—H6B	109.5	C12—C15—H15A	109.5
C5—C6—H6C	109.5	C12—C15—H15B	109.5
H6A—C6—H6C	109.5	H15A—C15—H15B	109.5
H6B—C6—H6C	109.5	C12—C15—H15C	109.5
C12—C7—C8	120.94 (14)	H15A—C15—H15C	109.5
C12—C7—N1	119.32 (14)	H15B—C15—H15C	109.5
C8—C7—N1	119.73 (14)		

C5—O2—C1—O1	−3.7 (2)	N1—C7—C8—C13	0.2 (2)
C5—O2—C1—C2	175.22 (15)	C7—C8—C9—C10	1.2 (2)
O1—C1—C2—C3	6.4 (3)	C13—C8—C9—C10	−178.42 (17)
O2—C1—C2—C3	−172.41 (15)	C8—C9—C10—C11	−0.6 (2)
C7—N1—C3—C2	−175.71 (16)	C8—C9—C10—C14	178.82 (16)
C7—N1—C3—C4	5.4 (3)	C9—C10—C11—C12	−0.2 (2)
C1—C2—C3—N1	−0.1 (3)	C14—C10—C11—C12	−179.62 (15)
C1—C2—C3—C4	178.75 (17)	C10—C11—C12—C7	0.4 (2)

C1—O2—C5—C6	−167.50 (15)	C10—C11—C12—C15	178.79 (16)
C3—N1—C7—C12	85.6 (2)	C8—C7—C12—C11	0.1 (2)
C3—N1—C7—C8	−95.9 (2)	N1—C7—C12—C11	178.62 (13)
C12—C7—C8—C9	−0.9 (2)	C8—C7—C12—C15	−178.23 (15)
N1—C7—C8—C9	−179.37 (13)	N1—C7—C12—C15	0.2 (2)
C12—C7—C8—C13	178.68 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.82 (2)	2.08 (2)	2.7516 (18)	138.7 (17)
N1—H1···O1^{i}	0.82 (2)	2.60 (2)	3.2201 (18)	133.1 (16)

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.