

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

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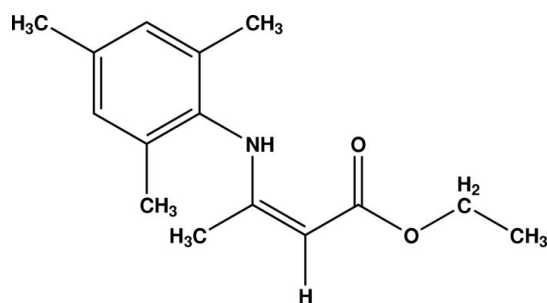
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
R factor = 0.049; wR factor = 0.145; data-to-parameter ratio = 15.9.

The title compound, $\text{C}_{15}\text{H}_{21}\text{NO}_2$, 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 = $88.10(6)^\circ$]. The molecular conformation is stabilized by a strong intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. In addition, the $\text{N}-\text{H}$ group forms a weak intermolecular $\text{N}-\text{H}\cdots\text{O}$ 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-inflammatory 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

$\text{C}_{15}\text{H}_{21}\text{NO}_2$
 $M_r = 247.33$
Monoclinic, $P2_1/c$
 $a = 8.5647(8)$ Å
 $b = 20.6131(19)$ Å
 $c = 8.2404(8)$ Å
 $\beta = 93.976(2)^\circ$

$V = 1451.3(2)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 298$ K
 $0.48 \times 0.37 \times 0.15$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

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, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.82 (2)	2.08 (2)	2.7516 (18)	138.7 (17)
$\text{N1}-\text{H1}\cdots\text{O1}^i$	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: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; 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).

References

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supplementary materials

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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-inflammatory 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 trimethylphenyl substituent is almost perpendicular to the β -enaminoester function forming a dihedral angle of 88.10 (6)°.

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 CH₂Cl₂ (3x10mL), dried (Na₂SO₄), filtered 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

Refinement

H atom on amine group was found in Fourier map and its coordinates were refined with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$. H atoms bonded to C atoms were placed in geometrically idealized positions [C-H = 0.97 Å (for CH₂) and 0.96 Å (for CH₃)] and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or 1.5 $U_{\text{eq}}(\text{C}(\text{methyl}))$.

Figures

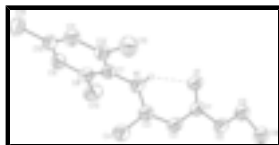


Fig. 1. The Molecular structure with the atom numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms bonded to C omitted. The intramolecular hydrogen bond is shown as a dashed line.

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

Crystal data

C₁₅H₂₁NO₂

$M_r = 247.33$

Monoclinic, $P2_1/c$

$F_{000} = 536$

$D_x = 1.132 \text{ Mg m}^{-3}$

Melting point: 338.2 K

supplementary materials

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) Å³
 $Z = 4$

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
 $0.48 \times 0.37 \times 0.15$ mm

Data collection

Bruker SMART APEX CCD
diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
Detector resolution: 0.661 pixels mm⁻¹
 $T = 298$ K
 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 25.4$ °
 $\theta_{\text{min}} = 2.0$ °
 $h = -10 \rightarrow 10$
 $k = -24 \rightarrow 24$
 $l = -9 \rightarrow 9$

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
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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³
Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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)

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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, °)

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 (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O1	0.82 (2)	2.08 (2)	2.7516 (18)	138.7 (17)
N1—H1 \cdots O1 ⁱ	0.82 (2)	2.60 (2)	3.2201 (18)	133.1 (16)

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

Fig. 1

