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Dimethyl (*Z*,*Z*)-3,3′-(propane-1,2-diyldiimino)dibut-2-enoate

Zhenfeng Zhang,[a] Shuo Jin,[a] Bo Liu[a] and Jianping Guo[b]*

[a]College of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, People's Republic of China, and [b]The Institute of Modern Chemistry, Shanxi University, Taiyuan 030006, People's Republic of China

Correspondence e-mail: g6391@yahoo.com

The title compound, $C_{13}H_{22}N_2O_4$, is a novel intermediate in the synthesis of related heterocycles. The molecule exhibits a *Z*,*Z* configuration, forming intramolecular N—H···O hydrogen bonds.

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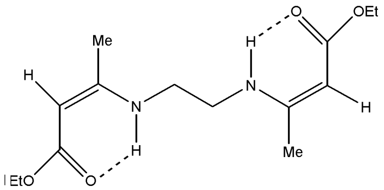
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.058
wR factor = 0.197
Data-to-parameter ratio = 15.7

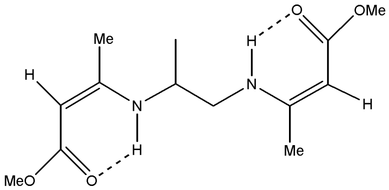
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

β-Enamino esters have been the subject of considerable research for some 30 years (Grigoryan & Agbalyan, 1973; Lulukyan *et al.*, 1982; Stefani *et al.*, 2000), because of their versatility and utility in organic synthesis. We had investigated the crystal structure of diethyl 3,3′-(ethane-1,2-diyldiimino)-dibut-2-enoate, (I), and found that the C═C bonds in (I) are in the *Z*,*Z* configuration, which is presumably formed by intramolecular hydrogen bonds of the N—H···O═C type (Zhang *et al.*, 2004). Based upon our observations and understanding of (I), we predicted that the novel compound (II) should still tend to form a *Z*,*Z* configuration. In order to validate our prediction and gain further insight into the structural features influencing the formation and reactivity, the crystal structure of the title compound, (II), has been determined.



(I)



(II)

The molecule has a conformation involving a twist of two moieties, *viz*. O1/C2/C3/C4/N1 and N2/C9/C11/C12/O3, which are both planar, with mean deviations of 0.0085 and 0.0095 Å, respectively (Fig. 1 and Table 1). The molecule adopts a *Z*,*Z* configuration around the bonds C3═C4 and C9═C11, which is shown to be governed by two relatively strong intramolecular hydrogen bonds of the N—H···O═C (acyl) type (Table 2). This configuration is identical to that found in other β-enamino esters (Zhang *et al.*, 2004; Smith & Taylor, 1979), indicating that the *Z* configuration is preferred for β-enamino esters.

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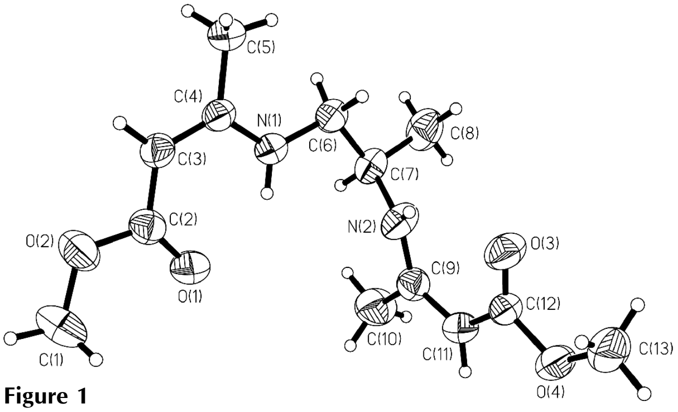

Figure 1
The molecular structure of (II), showing the atom-labeling scheme and 40% probability displacement ellipsoids.

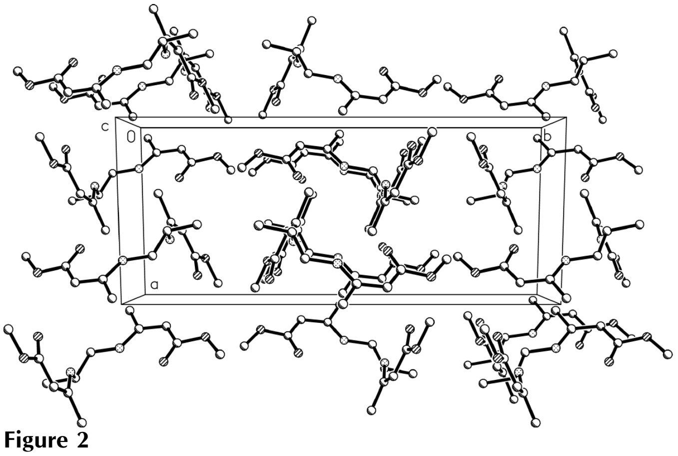

Figure 2
Packing diagram of (II), viewed along the *c* axis. H atoms have been omitted for clarity.

The bond distances of N1—C4 [1.340 (3) Å] and N2—C9 [1.334 (3) Å] in (II) are shorter than the standard C—N experimental bond length of 1.47 Å (Mak *et al.*, 2002), as is also observed in (I) (Zhang *et al.*, 2004). Conversely, the bond lengths of 1.368 (3) and 1.364 (3) Å found for C3═C4 and C9═C11 are longer than the normal C═C bond length of 1.32 Å (Mak *et al.*, 2002). The large deviations of these bond lengths from their normal values can be attributed to π-electron delocalization. The crystal structure is racemic, and the packing is shown in Fig. 2.

Experimental

Into a three-necked round-bottomed flask equipped with a mechanical stirrer were introduced methyl acetoacetate (0.5 mol) and water (50 ml). 1,2-Propanediamine (0.25 mol) was added in one portion and the flask was kept at room temperature under stirring for 20 min. The crude target compound was readily formed in the form of a colorless viscous oil. When the reaction mixture was cooled to room temperature, the oil layer was separated, washed with distilled water and dried over anhydrous calcium chloride, resulting in slow solidification. The product, (II), was recrystallized from ethyl acetate (yield 85%, m.p. 357–359 K). Spectroscopic analysis, ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.71 (*s*, 1H, $NHCH_2$), 8.54–8.51 (*d*, 1H, NHCH), 4.47 (*s*, 1H, ═CH), 4.45 (*s*, 1H, ═CH), 3.68–3.63 (*m*, 1H, CH_2CHCH_3), 3.62 (*s*, 6H, 2 × CH_3OCO), 3.26–3.21 (*t*, 2H, $NHCH_2CHCH_3$), 1.91 (*s*, 3H, ═CCH_3), 1.89 (*s*, 3H, ═CCH_3), 1.27–1.25 (*d*, 3H, CH_3CH).

Crystal data

$C_{13}H_{22}N_2O_4$
$M_r = 270.33$
Monoclinic, $P2_1/c$
$a = 8.7205\ (6)$ Å
$b = 20.2972\ (13)$ Å
$c = 8.8322\ (6)$ Å
$\beta = 102.295\ (1)°$
$V = 1527.46\ (18)$ Å^3
$Z = 4$
$D_x = 1.176$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3705 reflections
$\theta = 2.4–27.0°$
$\mu = 0.09$ mm^{-1}
$T = 293\ (2)$ K
Prism, colorless
0.60 × 0.40 × 0.40 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.917$, $T_{\max} = 0.966$
7560 measured reflections
2693 independent reflections
2178 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -24 \rightarrow 15$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.197$
$S = 1.11$
2693 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1057P)^2 + 0.4996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.220 (3)	N2—C9	1.334 (3)
O2—C2	1.356 (3)	C2—C3	1.419 (3)
O3—C12	1.212 (3)	C3—C4	1.368 (3)
O4—C12	1.353 (3)	C9—C11	1.364 (3)
N1—C4	1.340 (3)	C11—C12	1.422 (3)
O1—C2—C3—C4	1.7 (4)	N1—C6—C7—N2	−63.7 (3)
C6—N1—C4—C3	178.9 (2)	C7—N2—C9—C11	158.2 (2)
C4—N1—C6—C7	−174.6 (2)	C9—C11—C12—O3	3.1 (4)
C9—N2—C7—C6	152.7 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.86	2.07	2.729 (3)	133
N2—H2*A*···O3	0.86	2.15	2.731 (3)	125

H atoms were placed in their idealized positions (N—H = 0.86, C—H = 0.93–0.98 Å) and allowed to ride on the respective parent atoms, with $U_{\rm iso} = 1.2$ or $1.5U_{\rm eq}$(C,N).

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

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