Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Diethyl 3,8-dimethyl-4,7-diazadeca-2,8-dienedioate

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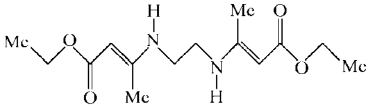
Received 21 April 2004
Accepted 1 July 2004
Online 11 August 2004

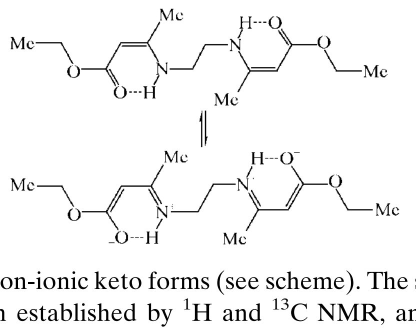
The title compound, $C_{14}H_{24}N_2O_4$, consists of two symmetric moieties related through a twofold axis. The whole molecule has a *cis* conformation. Both the ionic enol form and the non-ionic keto form make comparable contributions to the structure. In the crystal structure, infinite supramolecular chains are formed through N—H···O hydrogen bonds.

Comment

β-Enamino esters represent an important class of functionalized synthetic building blocks (Bartoli *et al.*, 2004). Recently, the title compound, (I), has been synthesized for the first time in our laboratory. According to a model of synergetic mutual reinforcement of hydrogen bonding and *π*-delocalization within a heterodienic system (Gilli *et al.*, 1989, 1993; Bertolasi *et al.*, 1991), (I) may be regarded as containing both the ionic enolic and non-ionic keto forms (see scheme). The structure of (I) has been established by ^{1}H and ^{13}C NMR, and IR spectroscopy, and has been fully confirmed by an X-ray structural analysis.



(I)



As shown in Fig. 1, compound (I) is built up from two asymmetric units related through a twofold axis. The whole molecule is arranged in a *cis* conformation with respect to the C6—C6($1-x, y, \frac{3}{2}-z$) bond. The C3═O1 bond [1.221 (2) Å] is shorter than a normal single C—O bond (*ca* 1.43 Å; Weininger & Stermitz, 1984), but longer than the double C═O bonds found in some esters, such as in an Amadori compound [1.189 (5) Å; Kojić-Prodić *et al.*, 1995], a benzoate [1.200 (4) Å; Huertas *et al.*, 1997] and a glycine derivative [1.186 (2) Å; Zhao *et al.*, 2002]. The N═C5 bond in (I) [1.344 (2) Å] is longer than a typical double C═N bond (*ca* 1.30 Å) but shorter than the C—N single bond [N—C6 = 1.443 (4) Å]. The C3—C4 bond length [1.425 (2) Å] is intermediate between a single C—C bond (*ca* 1.54 Å) and a C═C double bond (*ca* 1.34 Å). These features of the bond lengths in (I) indicate that both the ionic enolic and the non-ionic keto forms make comparable contributions to the structure.

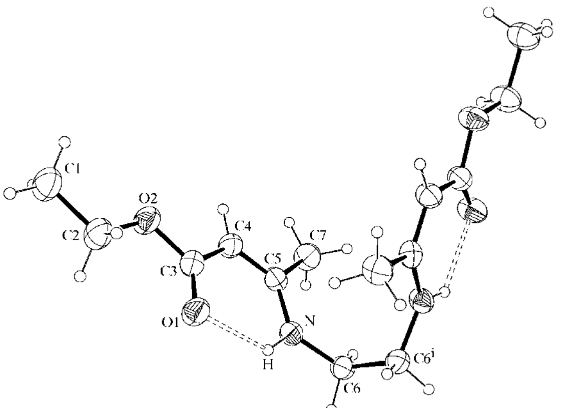


Figure 1
The formula unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are illustrated by dashed lines. [Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.]

The ^{1}H and ^{13}C NMR spectra show the olefinic resonances of atom C4 and its attached H atom at noticeably higher magnetic fields than normal, at 4.93 and 83.83 p.p.m., respectively. This indicates the contribution of the non-ionic keto form, which undergoes *π*-delocalization. On the other hand, the NH signal appears at a much lower magnetic field (8.64 p.p.m.) than normal in the ^{1}H NMR spectrum and this is indicative of the contribution of the ionic enolic form. These two forms are also observed in the related compound with an ethylenediimine (Özkar *et al.*, 2004), which shows almost the same deviations of the corresponding signals in the NMR spectra.

The IR spectroscopic data for (I) are consistent with the crystal structure. The absorption band centred at around 3297 cm^{-1} is readily ascribed to the NH group. The absorption band of C═O stretching at 1604 cm^{-1} appears to be lower than that for a typical C═O ketone group (1725–1705 cm^{-1}; Pine *et al.*, 1980) and is indicative of the ionic enolic form of the molecule.

The asymmetric unit of (I) is almost planar, with mean and maximum deviations of 0.0014 and 0.1330 Å, respectively, as the *π*-delocalization is reinforced by an N—H···O1 hydrogen bond. The sum of the angles around the N atom is close to 360°, indicating that the N atom is involved in the ionic enolic

DOI: 10.1107/S0108270104016130

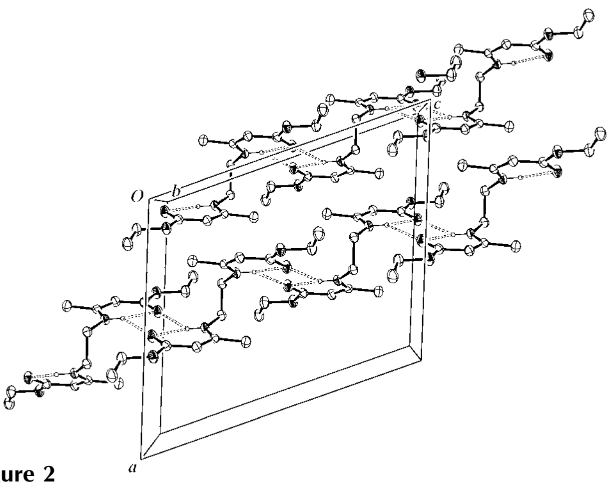


Figure 2
Part of the crystal structure of (I), showing the infinite hydrogen-bonded chains running along the [001] direction. H atoms have been omitted for clarity, except those involved in hydrogen bonds. Hydrogen bonds are illustrated by dashed lines.

form. In the solid state, the two halves of (I) are skewed, with a dihedral angle of 46.3° between them. In the structure, an infinite zigzag chain of molecules of (I) running along the [001] direction (Fig. 2) is built up *via* an N—H···O1($1-x$, $1-y$, $1-z$) hydrogen bond. These intermolecular hydrogen bonds form a ring which may be described as graph set $R_2^2(4)$ (Etter, 1990). This ring is embedded in the chain. There are no hydrogen bonds between separate chains. Duplication of the chain forms layers of (I) parallel to the (010) plane.

Experimental

Ethyl acetoacetate and ethylenediamine, in a molar ratio of 2:1, were mixed together and refluxed with stirring for 2 h. Crystals of (I) were formed by recrystallization of the resulting solid from ethanol, with a yield of approximately 65% based on ethyl acetoacetate. Spectroscopic analyses, IR (KBr, ν, cm^{-1}): 3297, 2984, 2953, 2898, 1604 (*br*), 1509, 1438, 1390, 1288, 1259, 1224, 1167 (*br*), 1115, 1092, 1067, 1021, 980, 784, 726, 566; ^{1}H NMR (CDCl$_3$, p.p.m.): 8.64 (1H, NH), 4.48 (1H, *s*, C4–H), 4.07 (2H, *q*, C2–H$_2$), 3.35 (2H, *s*, C6–H$_2$), 1.90 (3H, *s*, C7–H$_3$), 1.23 (3H, *t*, C1–H$_3$); ^{13}C NMR (CDCl$_3$, p.p.m.): 170.86 (C5), 161.55 (C3), 83.83 (C4), 58.72 (CH$_2$), 44.07 (CH$_2$), 19.49 (CH$_3$), 14.85 (CH$_3$).

Crystal data

$C_{14}H_{24}N_2O_4$
$M_r = 284.35$
Monoclinic, $C2/c$
$a = 11.734$ (3) Å
$b = 10.566$ (2) Å
$c = 13.418$ (3) Å
$\beta = 111.440$ (10)°
$V = 1548.5$ (6) Å^3
$Z = 4$

$D_x = 1.220$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 850 reflections
$\theta = 2.7$–20.2°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.25 × 0.15 × 0.15 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
4031 measured reflections

1520 independent reflections
946 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\max} = 26.0°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 8$
$l = -16 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.112$
$S = 0.91$
1520 reflections
93 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

C1—C2	1.479 (2)	C4—C5	1.356 (2)
C2—O2	1.436 (2)	C5—N	1.344 (2)
C3—O1	1.221 (2)	C5—C7	1.499 (2)
C3—O2	1.353 (2)	C6—N	1.445 (2)
C3—C4	1.425 (2)	C6—C6$^{\rm i}$	1.520 (3)

Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H···O1	0.86	2.14	2.784 (2)	132
N—H···O1$^{\rm i}$	0.86	2.67	3.292 (2)	130

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with an N—H distance of 0.86 Å and C—H distances in the range 0.93–0.97 Å, and with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$ for methyl H atoms and $1.2U_{\rm eq}({\rm C,N})$ for others.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1052). Services for accessing these data are described at the back of the journal.

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