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3-(Aminomethylene)pentane-2,4-dione

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.102
Data-to-parameter ratio = 17.5

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

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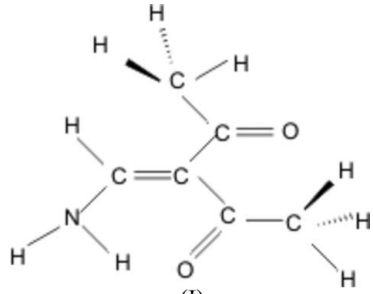
The orientations of NH_2 and CH_3 of the title compound, $C_6H_9NO_2$, are mainly stabilized by N—H···O and C—H···O intramolecular hydrogen bonds, as well as intermolecular N—H···O and C—H···O hydrogen bonds.

Comment

3-(Aminomethylene)pentane-2,4-dione, (I) (Fig. 1), belongs to the class of so-called push–pull olefins. Push–pull ethylenes are highly reactive organic compounds with the general formula $R_1X—CR_2{=}{=}CR_3R_4$, where R_1 and R_2 (for X = O and X = NH or NR_1) can be H or an alkyl or heteroaryl group, and R_3 and R_4 are strong electron-acceptor groups such as –CN, –CO*R* or –COO*R* (Cook, 1969). Enamines (X = NH or N*R*) are frequently used in chemical syntheses of drugs, polymers and dyes (Dyke, 1973). Properties such as polar character, electronic interactions between substituents and the double bond are responsible for their non-linear optical properties and their use as new electro-optical materials (Kolev *et al.*, 2003).



(I)

The orientations of the NH_2 and CH_3 groups of compound (I) are mainly stabilized by intramolecular N—H···O and C—H···O hydrogen bonds, as well as intermolecular N—H···O and C—H···O hydrogen bonds (Table 1).

Experimental

To 3-methoxymethylenepentane-2,4-dione (1.42 g, 10 mmol) or 3-ethoxymethylenepentane-2,4-dione (1.56 g, 10 mmol) in methanol (10 ml) (ethanol for the ethoxy derivative), an aqueous solution of ammonia (12 mmol) was added dropwise (amount according to concentration and density) over a period of 30 min with stirring. The slightly warmed mixture was stirred overnight at room temperature. The reaction mixture was then briefly heated to reflux (*ca* 20 min). After ensuring that no starting derivative remained (thin-layer chromatography; Silufol 254, Kavalier Czechoslovakia; eluent chloroform–methanol 10:1 *v*/*v*, detection UV light 254 nm), the reaction mixture was evaporated on a vacuum evaporator and

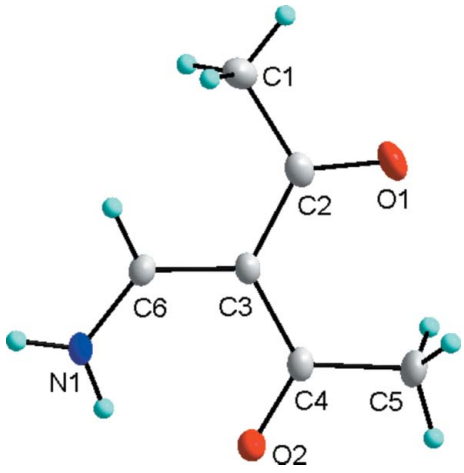


Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

chromatographed on silica gel (eluent dichloromethane–methanol 10:1 *v*/*v*).

Crystal data

$C_6H_9NO_2$	V = 1322.0 (4) Å^3
M_r = 127.14	Z = 8
Monoclinic, $C2/c$	D_x = 1.278 Mg m^{-3}
a = 6.924 (2) Å	Mo $K\alpha$ radiation
b = 13.396 (2) Å	μ = 0.10 mm^{-1}
c = 14.6300 (10) Å	T = 100 K
β = 103.030 (10)°	Block, colourless
β = 103.030 (10)°	0.55 × 0.16 × 0.04 mm

Data collection

Oxford Diffraction GEMINI R diffractometer	6668 measured reflections
ω and φ scans	1537 independent reflections
Absorption correction: analytical (Clark & Reid, 1995)	1027 reflections with $I > 2\sigma(I)$
T_{min} = 0.898, T_{max} = 1.000	R_{int} = 0.028
	θ_{max} = 29.0°

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.102	$(\Delta/\sigma)_{max} < 0.001$
S = 0.98	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
1537 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
88 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2B···O2	0.86	2.02	2.627 (2)	127
C5—H5A···O1	0.96	2.53	2.761 (1)	93
C5—H5B···O1	0.96	2.52	2.761 (1)	94
N1—H2A···O1^{i}	0.86	1.95	2.795 (1)	166
N1—H2B···O2^{ii}	0.86	2.26	2.939 (1)	136

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y, -z+1$.

Olefinic and amino H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms at distances of 0.93 and 0.86 Å, respectively, with U_{iso}(H) = 1.2U_{eq}(C,N). Methyl H atoms were located in a difference Fourier map and included in the model as a rigid rotating group, with C—H distances of 0.96 Å and with U_{iso}(H) = 1.5U_{eq}(C).

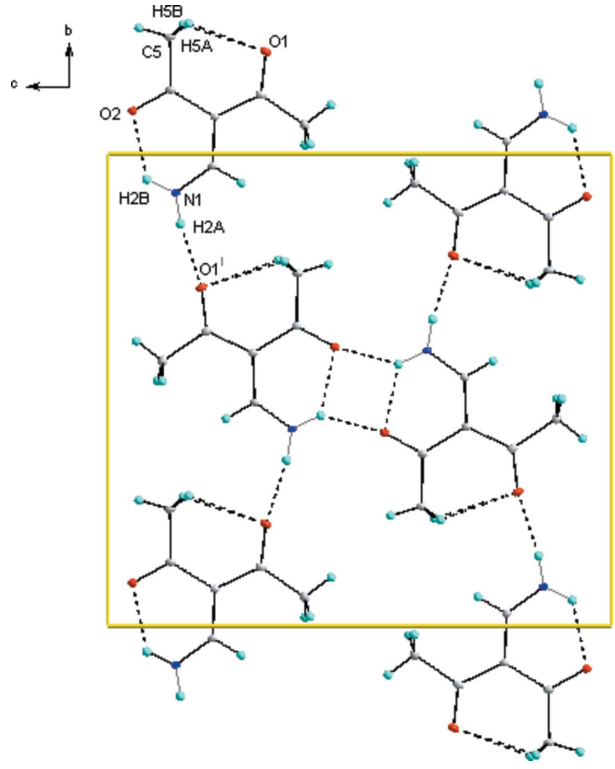


Figure 2
A packing diagram for (I), viewed along the *a* axis. Hydrogen-bond interactions are indicated by dashed lines.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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