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Methylmalonamide and ethylmalonamide

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In the title compounds, $C_4H_8N_2O_2$, (I), and $C_5H_{10}N_2O_2$, (II), respectively, the amide groups are rotated out of the central C—C—C plane by *ca* 76° in (I) and by 70–73° in (II). Compound (I) has crystallographic mirror symmetry perpendicular to the molecular plane.

Comment

The malonamides have a stronger extracting capacity than other diamides, which is due to the larger electron delocalization and the higher chelating abilities of malonamides (Siddall & Good, 1967). The title substituted malonamides, (I) and (II), were synthesized with the aim of studying their lipophilic suitability as extractants. The crystal structure analyses of (I) and (II) revealed different space groups, namely orthorhombic *Pnma* for (I) and monoclinic $P2_1/n$ for (II). In the molecular structure of (I), the molecule is bisected
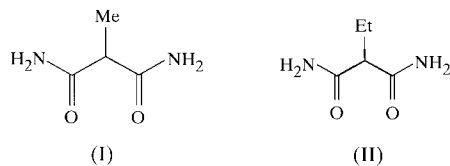
by a mirror plane passing through atoms H5, C3, C1 and H3. Bond lengths and angles are in the usual ranges. There are N—H⋯O intermolecular hydrogen bonds in (I), and N—H⋯O and C—H⋯O intermolecular hydrogen bonds in (II). In both title compounds, each amide O atom acts as an acceptor in two hydrogen bonds. These hydrogen bonds stabilize the intermolecular packing (Tables 1 and 2).

Experimental

A suspension of substituted diethyl malonate and NH_3 solution was refluxed for one week with vigorous stirring. Crystals of (I) and (II) were obtained by slow evaporation of an ethanol solution.

Compound (I)

Crystal data

$C_4H_8N_2O_2$	Mo $K\alpha$ radiation
$M_r = 116.12$	Cell parameters from 25
Orthorhombic, *Pnma*	reflections
$a = 9.778\,(2)$ Å	$\theta = 13.8–14.9°$
$b = 10.879\,(2)$ Å	$\mu = 0.102$ mm^{-1}
$c = 5.706\,(2)$ Å	$T = 296.2$ K
$V = 607.0\,(2)$ Å^3	Prismatic, colorless
$Z = 4$	$0.25 \times 0.20 \times 0.10$ mm
$D_x = 1.271$ Mg m^{-3}	

Data collection

Rigaku AFC-5R diffractometer	$\theta_{max} = 27.51°$
ω–2θ scans	$h = -12 \to 0$
Absorption correction: ψ scan	$k = 0 \to 14$
(North *et al.*, 1968)	$l = 0 \to 7$
$T_{min} = 0.980$, $T_{max} = 0.997$	3 standard reflections
854 measured reflections	every 150 reflections
735 independent reflections	intensity decay: 3.48%
451 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	All H-atom parameters refined
$R(F) = 0.0404$	$w = 1/(\sigma^2(F_o^2) + \{0.050[\text{Max}(F_o^2,0)$
$wR(F^2) = 0.1146$	$+ 2F_c^2]/3\}^2)$
$S = 1.152$	$(\Delta/\sigma)_{max} = 0.0019$
735 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
58 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1^i	0.91 (2)	1.97 (2)	2.8445 (18)	162 (2)
N1—H2⋯O1^{ii}	0.97 (2)	1.987 (19)	2.943 (2)	169.4 (17)

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

Compound (II)

Crystal data

$C_5H_{10}N_2O_2$	$D_x = 1.264$ Mg m^{-3}
$M_r = 130.15$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 6.570\,(1)$ Å	reflections
$b = 9.502\,(1)$ Å	$\theta = 12.8–13.5°$
$c = 11.032\,(1)$ Å	$\mu = 0.098$ mm^{-1}
$\beta = 96.69\,(1)°$	$T = 296.2$ K
$V = 684.1\,(2)$ Å^3	Prismatic, colorless
$Z = 4$	$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.029$
ω–2θ scans	$\theta_{max} = 27.57°$
Absorption correction: ψ scan	$h = 0 \to 8$
(North *et al.*, 1968)	$k = 0 \to 12$
$T_{min} = 0.974$, $T_{max} = 0.998$	$l = -14 \to 14$
1830 measured reflections	3 standard reflections
1589 independent reflections	every 150 reflections
1077 reflections with $I > 2\sigma(I)$	intensity decay: 0.50%

Refinement

Refinement on F^2	All H-atom parameters refined
$R(F) = 0.051$	$w = 1/(\sigma^2(F_o^2) + \{0.048[\text{Max}(F_o^2,0)$
$wR(F^2) = 0.120$	$+ 2F_c^2]/3\}^2)$
$S = 1.131$	$(\Delta/\sigma)_{max} = 0.0033$
1589 reflections	$\Delta\rho_{max} = 0.60$ e Å^{-3}
121 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H4$\cdots$O2^i	0.85 (3)	2.08 (3)	2.906 (2)	164 (2)
N2—H3$\cdots$O1^{ii}	0.90 (2)	2.10 (2)	2.996 (2)	174.5 (18)
N1—H1$\cdots$O1^i	0.90 (3)	1.98 (3)	2.859 (2)	165 (2)
N1—H2$\cdots$O2^{iii}	0.85 (2)	2.14 (2)	2.982 (2)	167.1 (19)
C1—H5$\cdots$O2^i	0.967 (19)	2.59 (2)	3.441 (2)	147.5 (17)

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

All the H atoms were located from the difference Fourier map and refined isotropically. In (I), the C—H range is 0.95 (3)–0.96 (3) Å and the N—H range is 0.90 (2)–0.96 (2) Å. In (II), the C—H range is 0.95 (3)–1.00 (3) Å and the N—H range is 0.85 (3)–0.91 (2) Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduc-

tion: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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