

Dimethyl 2-(methylaminomethylene)-malonate

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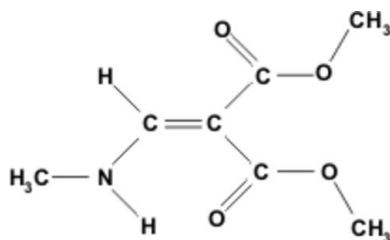
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.092; wR factor = 0.257; data-to-parameter ratio = 20.8.

In the title compound, $\text{C}_7\text{H}_{11}\text{NO}_4$, which is an example of a push-pull alkene, a network of $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions helps to establish the crystal structure. The investigated crystal turned out to be a non-merohedral twin with a ratio of twin components of 0.442 (3):0.558 (3). Two pairs of independent molecules ($Z' = 4$) are linked by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming independent chains; the chains are connected *via* intermolecular $\text{C}-\text{H}\cdots\text{O}$ contacts, building a three-dimensional network.

Related literature

For related literature, see: Bouzard (1990); Cook (1969); Dyke (1973); Freeman (1981); Gróf *et al.* (2008); Kálmán & Argay (1998); Bolte (2004).



Experimental

Crystal data

$\text{C}_7\text{H}_{11}\text{NO}_4$	$\gamma = 94.02$ (3)°
$M_r = 173.17$	$V = 1618.1$ (6) Å ³
Triclinic, $P\bar{1}$	$Z = 8$
$a = 11.165$ (2) Å	Mo $K\alpha$ radiation
$b = 12.073$ (2) Å	$\mu = 0.12$ mm ⁻¹
$c = 13.211$ (3) Å	$T = 100$ K
$\alpha = 113.70$ (3)°	$0.43 \times 0.15 \times 0.08$ mm
$\beta = 93.71$ (3)°	

Data collection

Oxford Diffraction GEMINI R diffractometer	Diffraction, 2006)
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford)	$T_{\min} = 0.968$, $T_{\max} = 0.996$
	9295 measured reflections
	9295 independent reflections
	3920 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.091$	96 restraints
$wR(F^2) = 0.257$	H-atom parameters constrained
$S = 0.90$	$\Delta\rho_{\max} = 1.13$ e Å ⁻³
9295 reflections	$\Delta\rho_{\min} = -0.54$ e Å ⁻³
446 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.86	2.08	2.689 (4)	127
$\text{N1}-\text{H1}\cdots\text{O10}$	0.86	2.42	2.990 (4)	125
$\text{N2}-\text{H2}\cdots\text{O5}$	0.86	2.08	2.687 (4)	127
$\text{N2}-\text{H2}\cdots\text{O14}^i$	0.86	2.30	2.893 (5)	127
$\text{N3}-\text{H3}\cdots\text{O9}$	0.86	2.06	2.684 (4)	129
$\text{N3}-\text{H3}\cdots\text{O2}^i$	0.86	2.32	2.912 (5)	126
$\text{N4}-\text{H4}\cdots\text{O13}$	0.86	2.08	2.698 (5)	128
$\text{N4}-\text{H4}\cdots\text{O6}$	0.86	2.40	2.957 (5)	123
$\text{C4}-\text{H4A}\cdots\text{O2}$	0.93	2.27	2.683 (7)	106
$\text{C6}-\text{H6A}\cdots\text{O14}$	0.96	2.50	3.449 (7)	169
$\text{C11}-\text{H11A}\cdots\text{O6}$	0.93	2.29	2.706 (6)	107
$\text{C11}-\text{H11A}\cdots\text{O13}$	0.93	2.60	3.487 (6)	159
$\text{C14}-\text{H14A}\cdots\text{O13}$	0.96	2.59	3.507 (6)	161
$\text{C18}-\text{H18A}\cdots\text{O1}$	0.93	2.58	3.470 (6)	160
$\text{C18}-\text{H18A}\cdots\text{O10}$	0.93	2.27	2.679 (6)	106
$\text{C25}-\text{H25A}\cdots\text{O14}$	0.93	2.28	2.691 (6)	106
$\text{C27}-\text{H27A}\cdots\text{O2}^i$	0.96	2.59	3.340 (7)	135
$\text{C28}-\text{H28C}\cdots\text{O6}$	0.96	2.60	3.024 (6)	107

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2088).

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Acta Cryst. (2008). E64, o1133-o1134 [doi:10.1107/S1600536808014773]

Dimethyl 2-(methylaminomethylene)malonate

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Comment

The title compound, C₇H₁₁N O₄, belongs to the so-called push-pull olefins. Push-pull alkenes are substituted ethylenes containing electron-donor groups (D) at one end and electron-acceptor groups (A) at the other end of the general formula D¹D²C=CA¹A². These compounds very often contain alkoxy, amino, alkylamino, dialkylamino or (hetero)aryl groups as electron-donor groups and cyano, acetyl, alkylester, methylsulfonyl or NO₂ groups as electron-acceptor groups. They are useful as starting reactants or intermediates for a lot of pharmaceutical, polymer and other syntheses (Cook, 1969; Dyke, 1973). Mainly enamines are frequently used as reactants or intermediates in chemical syntheses of drugs, polymers and dyes (Bouzard, 1990). But also alkoxyethylenes are often used in organic synthesis (Freeman, 1981).

Chemical and physical properties of the title related structures were recently discussed (Gróf *et al.*, 2008 and literature cited therein).

The study of a similar compound, dimethyl 2-(aminomethylene)malonate, (Gróf *et al.*, 2008) revealed that this structure exists in the solid phase as EZ conformer (E denotes away from C=C double bond orientation of the carbonyl oxygen in *trans* position; Z denotes towards to C=C double bond orientation of the carbonyl oxygen in *cis* position). The title compound exists in the solid phase as ZZa conformer (a denotes anti orientation of the methylamino group, *e.g.* away from the C=C double bond orientation).

The molecules I and II, and molecules III and IV of the title compound (Fig.1) show pseudo translation (Kálmán & Argay, (1998).

Experimental

To dimethyl 3-methoxymethylenemalonate (1.74 g, 10 mmol) in methanol (10 ml), an aqueous solution of methylamine (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 chromatographed on silica gel (eluent dichloromethane-methanol 10:1 v/v). Obtained product was recrystallized from minimal amount of chloroform and n-hexane mixture in refrigerator.

The solid phase mid-IR vibrational spectrum was recorded with a Nicolet model NEXUS 470 FTIR spectrometer at room temperature. The measurement was performed after mixing the powdered sample with KBr into a pellet.

The mid-IR vibrational frequencies of dimethyl 2-(methylaminomethylene)malonate are (in cm⁻¹): 3301 m; 3199 w, sh, b; 3092 vw; 3052 vw; 3039 vw; 3013 w; 2999 w; 2951 m; 2924 w, sh; 2905 vw, sh; 1701 vw, sh; 1680 v s; 1651 vw, sh; 1631 v s; 1612 w, sh; 1541 vw; 1478 w; 1450 m; 1430 m; 1405 m; 1360 s; 1330 vw, sh; 1322 m; 1281 s; 1225 s; 1187

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m; 1151 s; 1082 m; 1042 w; 1018 m; 998 w; 942 vw; 837 vw, sh; 820 s; 808 s; 768 m; 759 vw, sh; 671 m; 579 w, b; 459 vw; 446 vw; 413 m.

Refinement

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. Methyl H atoms were located in a difference Fourier map and included in the model as a rigid rotating group, with C—H distance of 0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

The investigated crystal was a non-merohedral twin. Two orientation matrices could be determined and the twin law was derived using the program TWINLAW (Bolte, 2004):

$$h(\text{twin}) = (1.00 * h) + (0.00 * k) + (0.00 * l)$$

$$k(\text{twin}) = (-0.15 * h) + (-1.00 * k) + (0.00 * l)$$

$$l(\text{twin}) = (-0.16 * h) + (0.00 * k) + (-1.00 * l).$$

For the refinement the reflection data file was modified using the program HKLF5 (Bolte, 2004). The contribution of the minor twin component refined to 0.442 (3).

Figures

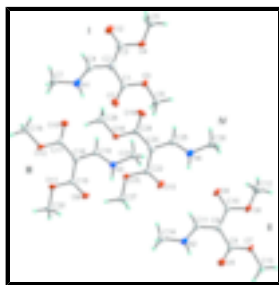


Fig. 1. The atom-numbering scheme of dimethyl 2-(methylaminomethylene)malonate. Displacement ellipsoids are drawn at the 60% probability level.

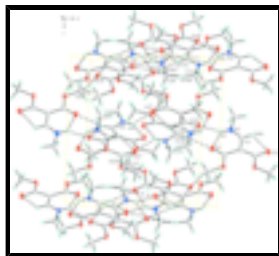


Fig. 2. Packing diagram of dimethyl 2-(methylaminomethylene)malonate. Hydrogen-bond interactions are indicated by dashed lines.

Dimethyl 2-(methylaminomethylene)malonate

Crystal data

$\text{C}_7\text{H}_{11}\text{NO}_4$

$M_r = 173.17$

Triclinic, $P\bar{1}$

$Z = 8$

$F_{000} = 736$

$D_x = 1.422 \text{ Mg m}^{-3}$

Hall symbol: -P 1

$a = 11.165$ (2) Å

$b = 12.073$ (2) Å

$c = 13.211$ (3) Å

$\alpha = 113.70$ (3)°

$\beta = 93.71$ (3)°

$\gamma = 94.02$ (3)°

$V = 1618.1$ (6) Å³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2135 reflections

$\theta = 3.3$ – 29.5 °

$\mu = 0.12$ mm⁻¹

$T = 100$ K

Block, yellow

$0.43 \times 0.15 \times 0.08$ mm

Data collection

Oxford Diffraction GEMINI R
diffractometer

9295 independent reflections

Radiation source: fine-focus sealed tube

3920 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$R_{\text{int}} = 0.0000$

$T = 100$ K

$\theta_{\text{max}} = 25.4$ °

Rotation method data acquisition using ω and φ scans $\theta_{\text{min}} = 4.1$ °

Absorption correction: analytical
(CrysAlis RED; Oxford Diffraction, 2006)

$h = -13$ → 13

$T_{\text{min}} = 0.968$, $T_{\text{max}} = 0.996$

$k = -14$ → 14

9295 measured reflections

$l = -15$ → 15

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.092$

H-atom parameters constrained

$wR(F^2) = 0.257$

$w = 1/[\sigma^2(F_o^2) + (0.1527P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 0.90$

$(\Delta/\sigma)_{\text{max}} = 0.067$

9295 reflections

$\Delta\rho_{\text{max}} = 1.13$ e Å⁻³

446 parameters

$\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

96 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

Special details

Experimental. face-indexed (CrysAlis RED; Oxford Diffraction, 2006). 96 rigid bond restraints (DELU) were used in the refinement because the data to parameter ratio is low due to four independent molecules in the twinned structure.

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.

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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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.0504 (4)	0.1221 (5)	0.6433 (4)	0.0202 (11)
C2	1.1715 (5)	0.1334 (5)	0.6103 (4)	0.0234 (11)
C3	1.2819 (5)	0.1043 (5)	0.6504 (4)	0.0238 (11)
C4	1.1851 (5)	0.1766 (5)	0.5297 (4)	0.0274 (12)
H4A	1.2634	0.1815	0.5106	0.033*
C5	1.3825 (4)	0.0278 (5)	0.7690 (4)	0.0327 (14)
H5C	1.3656	-0.0079	0.8203	0.039*
H5B	1.4350	0.1019	0.8066	0.039*
H5A	1.4210	-0.0279	0.7090	0.039*
C6	0.9264 (4)	0.0767 (5)	0.7613 (4)	0.0241 (12)
H6C	0.9311	0.0528	0.8224	0.029*
H6B	0.8723	0.0182	0.7012	0.029*
H6A	0.8970	0.1552	0.7848	0.029*
C7	1.1353 (4)	0.2577 (5)	0.3932 (4)	0.0298 (13)
H7C	1.1168	0.3404	0.4176	0.036*
H7B	1.0889	0.2087	0.3236	0.036*
H7A	1.2198	0.2546	0.3840	0.036*
O1	0.9618 (3)	0.1470 (3)	0.6036 (3)	0.0317 (9)
O2	1.3803 (3)	0.1235 (3)	0.6240 (3)	0.0294 (9)
O3	1.0441 (3)	0.0828 (3)	0.7250 (3)	0.0257 (8)
O4	1.2710 (3)	0.0540 (3)	0.7254 (3)	0.0303 (9)
N1	1.1056 (4)	0.2113 (4)	0.4763 (3)	0.0290 (11)
H1	1.0317	0.2069	0.4902	0.035*
C8	0.0163 (4)	0.1936 (5)	1.0767 (4)	0.0227 (11)
C9	0.1389 (4)	0.2097 (5)	1.0475 (4)	0.0198 (10)
C10	0.2442 (4)	0.1583 (5)	1.0733 (4)	0.0234 (11)
C11	0.1614 (4)	0.2782 (5)	0.9871 (4)	0.0224 (11)
H11A	0.2405	0.2835	0.9699	0.027*
C12	0.3325 (4)	0.0431 (6)	1.1587 (4)	0.0374 (14)
H12C	0.3077	-0.0189	1.1835	0.045*
H12B	0.3855	0.1061	1.2165	0.045*
H12A	0.3742	0.0082	1.0936	0.045*
C13	-0.1214 (4)	0.1026 (5)	1.1526 (4)	0.0261 (13)
H13C	-0.1269	0.0428	1.1833	0.031*
H13B	-0.1767	0.0763	1.0866	0.031*
H13A	-0.1415	0.1788	1.2061	0.031*
C14	0.1222 (4)	0.3979 (5)	0.8809 (4)	0.0231 (12)
H14C	0.1054	0.4812	0.9146	0.028*
H14B	0.0770	0.3583	0.8092	0.028*
H14A	0.2068	0.3949	0.8728	0.028*

O5	-0.0631 (3)	0.2510 (3)	1.0591 (3)	0.0302 (9)
O6	0.3444 (3)	0.1722 (3)	1.0442 (3)	0.0350 (10)
O7	-0.0002 (3)	0.1176 (3)	1.1253 (3)	0.0272 (9)
O8	0.2281 (3)	0.0937 (3)	1.1328 (3)	0.0290 (9)
N2	0.0879 (3)	0.3365 (4)	0.9506 (3)	0.0262 (10)
H2	0.0153	0.3386	0.9690	0.031*
C15	0.5457 (4)	0.3104 (5)	0.4300 (4)	0.0228 (11)
C16	0.6700 (4)	0.2928 (5)	0.4565 (4)	0.0211 (11)
C17	0.7792 (4)	0.3434 (5)	0.4301 (4)	0.0233 (11)
C18	0.6930 (4)	0.2229 (5)	0.5142 (4)	0.0205 (11)
H18A	0.7734	0.2125	0.5271	0.025*
C19	0.8722 (4)	0.4640 (5)	0.3477 (4)	0.0289 (13)
H19C	0.8530	0.5219	0.3178	0.035*
H19B	0.9068	0.3981	0.2930	0.035*
H19A	0.9291	0.5030	0.4126	0.035*
C20	0.4082 (4)	0.4033 (5)	0.3540 (4)	0.0277 (13)
H20C	0.4074	0.4651	0.3257	0.033*
H20B	0.3676	0.4278	0.4203	0.033*
H20A	0.3677	0.3284	0.2992	0.033*
C21	0.6479 (4)	0.1022 (5)	0.6200 (4)	0.0203 (11)
H21C	0.6040	0.0227	0.5890	0.024*
H21B	0.6293	0.1455	0.6949	0.024*
H21A	0.7329	0.0947	0.6197	0.024*
O9	0.4592 (3)	0.2600 (3)	0.4495 (3)	0.0293 (9)
O10	0.8808 (3)	0.3234 (3)	0.4529 (3)	0.0315 (9)
O11	0.5322 (3)	0.3861 (3)	0.3795 (3)	0.0255 (8)
O12	0.7640 (3)	0.4176 (3)	0.3774 (3)	0.0276 (9)
N3	0.6133 (3)	0.1691 (4)	0.5531 (3)	0.0231 (10)
H3	0.5379	0.1732	0.5389	0.028*
C22	0.5158 (4)	0.3785 (5)	0.8567 (4)	0.0194 (10)
C23	0.6390 (5)	0.3641 (5)	0.8899 (4)	0.0239 (11)
C24	0.7487 (4)	0.3923 (5)	0.8491 (4)	0.0208 (11)
C25	0.6589 (4)	0.3189 (5)	0.9702 (4)	0.0240 (11)
H25A	0.7389	0.3117	0.9884	0.029*
C26	0.8480 (4)	0.4731 (5)	0.7386 (4)	0.0313 (14)
H26C	0.8301	0.5026	0.6823	0.038*
H26B	0.8883	0.4010	0.7078	0.038*
H26A	0.8992	0.5344	0.7993	0.038*
C27	0.3829 (4)	0.4259 (5)	0.7369 (4)	0.0283 (13)
H27C	0.3840	0.4511	0.6767	0.034*
H27B	0.3486	0.4854	0.7977	0.034*
H27A	0.3352	0.3488	0.7126	0.034*
C28	0.6131 (4)	0.2394 (5)	1.1070 (4)	0.0288 (13)
H28C	0.5723	0.1594	1.0857	0.035*
H28B	0.5901	0.2928	1.1776	0.035*
H28A	0.6988	0.2357	1.1127	0.035*
O13	0.4292 (3)	0.3554 (3)	0.8977 (3)	0.0285 (9)
O14	0.8494 (3)	0.3706 (3)	0.8760 (3)	0.0303 (9)
O15	0.5064 (3)	0.4145 (3)	0.7733 (3)	0.0274 (9)

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O16	0.7371 (3)	0.4453 (3)	0.7781 (3)	0.0281 (9)
N4	0.5799 (3)	0.2852 (4)	1.0234 (3)	0.0279 (11)
H4	0.5048	0.2902	1.0087	0.033*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0197 (14)	0.022 (3)	0.023 (3)	-0.001 (2)	0.0012 (18)	0.015 (2)
C2	0.0238 (14)	0.027 (3)	0.028 (3)	0.004 (2)	0.010 (2)	0.018 (2)
C3	0.0194 (13)	0.024 (3)	0.032 (3)	-0.005 (2)	0.0010 (19)	0.016 (2)
C4	0.025 (2)	0.038 (4)	0.028 (3)	0.001 (2)	0.0052 (19)	0.021 (2)
C5	0.017 (2)	0.051 (4)	0.037 (3)	0.010 (3)	0.002 (2)	0.024 (3)
C6	0.016 (2)	0.029 (3)	0.033 (3)	0.003 (2)	0.010 (2)	0.017 (3)
C7	0.019 (3)	0.047 (4)	0.039 (3)	0.007 (3)	0.008 (2)	0.032 (3)
O1	0.0238 (14)	0.045 (3)	0.039 (2)	0.0054 (18)	0.0020 (16)	0.0304 (19)
O2	0.0227 (13)	0.035 (2)	0.037 (2)	0.0020 (17)	0.0098 (15)	0.0208 (19)
O3	0.0162 (16)	0.041 (2)	0.033 (2)	0.0036 (16)	0.0077 (14)	0.0271 (17)
O4	0.0117 (16)	0.050 (3)	0.043 (2)	0.0040 (16)	0.0044 (14)	0.0333 (18)
N1	0.022 (2)	0.040 (3)	0.037 (3)	0.000 (2)	0.0054 (17)	0.028 (2)
C8	0.0168 (15)	0.033 (3)	0.030 (3)	0.004 (2)	0.009 (2)	0.023 (2)
C9	0.0169 (15)	0.028 (3)	0.021 (3)	0.0014 (19)	0.009 (2)	0.015 (2)
C10	0.0171 (15)	0.039 (3)	0.024 (3)	0.004 (2)	0.009 (2)	0.022 (2)
C11	0.012 (2)	0.032 (3)	0.032 (3)	-0.0026 (19)	0.0027 (19)	0.022 (2)
C12	0.023 (3)	0.056 (4)	0.048 (4)	0.015 (3)	0.005 (3)	0.034 (3)
C13	0.014 (2)	0.037 (4)	0.038 (3)	0.002 (2)	0.010 (2)	0.026 (3)
C14	0.023 (3)	0.028 (3)	0.023 (3)	0.002 (2)	0.005 (2)	0.015 (2)
O5	0.0174 (15)	0.045 (3)	0.042 (2)	0.0075 (16)	0.0068 (16)	0.0311 (19)
O6	0.0161 (14)	0.058 (3)	0.050 (2)	0.0019 (18)	0.0111 (17)	0.041 (2)
O7	0.0144 (16)	0.043 (2)	0.040 (2)	0.0013 (15)	0.0094 (15)	0.0329 (18)
O8	0.0155 (17)	0.049 (3)	0.042 (2)	0.0103 (16)	0.0146 (15)	0.0355 (18)
N2	0.013 (2)	0.039 (3)	0.039 (3)	0.0046 (18)	0.0077 (18)	0.028 (2)
C15	0.0119 (11)	0.033 (3)	0.030 (3)	-0.0031 (19)	-0.005 (2)	0.022 (2)
C16	0.0128 (11)	0.032 (3)	0.027 (3)	0.0031 (19)	0.001 (2)	0.021 (2)
C17	0.0135 (12)	0.040 (3)	0.026 (3)	0.003 (2)	0.003 (2)	0.023 (2)
C18	0.012 (2)	0.031 (3)	0.025 (3)	0.0008 (19)	0.0000 (19)	0.019 (2)
C19	0.012 (2)	0.040 (4)	0.043 (3)	-0.004 (2)	0.005 (2)	0.026 (3)
C20	0.0096 (19)	0.041 (4)	0.042 (3)	0.003 (2)	-0.003 (2)	0.026 (3)
C21	0.013 (3)	0.029 (3)	0.025 (3)	-0.001 (2)	0.002 (2)	0.017 (2)
O9	0.0130 (12)	0.044 (2)	0.042 (2)	-0.0022 (16)	-0.0003 (16)	0.0305 (19)
O10	0.0138 (11)	0.051 (3)	0.044 (2)	0.0069 (16)	0.0047 (16)	0.033 (2)
O11	0.0089 (15)	0.041 (2)	0.040 (2)	0.0046 (14)	0.0015 (14)	0.0301 (18)
O12	0.0089 (16)	0.039 (2)	0.047 (2)	-0.0023 (14)	0.0013 (15)	0.0319 (18)
N3	0.013 (2)	0.030 (3)	0.036 (3)	0.0008 (17)	0.0019 (17)	0.022 (2)
C22	0.0149 (12)	0.021 (3)	0.028 (3)	-0.005 (2)	0.0005 (17)	0.017 (2)
C23	0.0187 (12)	0.033 (4)	0.026 (3)	0.002 (2)	0.0005 (19)	0.018 (2)
C24	0.0151 (13)	0.023 (3)	0.031 (3)	0.002 (2)	-0.0005 (19)	0.018 (2)
C25	0.017 (2)	0.032 (3)	0.030 (3)	0.002 (2)	0.0029 (18)	0.019 (2)
C26	0.020 (2)	0.042 (4)	0.033 (3)	-0.007 (3)	0.006 (2)	0.019 (3)

C27	0.0096 (19)	0.045 (4)	0.040 (3)	0.000 (2)	-0.001 (2)	0.028 (3)
C28	0.016 (3)	0.044 (4)	0.040 (3)	0.004 (2)	0.009 (2)	0.029 (3)
O13	0.0200 (13)	0.040 (2)	0.035 (2)	-0.0019 (17)	0.0086 (15)	0.0246 (18)
O14	0.0181 (12)	0.040 (3)	0.040 (2)	0.0072 (17)	-0.0039 (15)	0.0246 (19)
O15	0.0099 (15)	0.048 (3)	0.039 (2)	-0.0001 (16)	0.0013 (14)	0.0338 (19)
O16	0.0100 (16)	0.047 (3)	0.043 (2)	0.0014 (16)	0.0000 (14)	0.0347 (18)
N4	0.018 (2)	0.035 (3)	0.041 (3)	-0.0015 (19)	0.0029 (17)	0.026 (2)

Geometric parameters (Å, °)

C1—O1	1.202 (5)	C15—O9	1.204 (5)
C1—O3	1.346 (5)	C15—O11	1.341 (6)
C1—C2	1.461 (6)	C15—C16	1.460 (6)
C2—C4	1.373 (6)	C16—C18	1.372 (6)
C2—C3	1.432 (7)	C16—C17	1.450 (7)
C3—O2	1.208 (5)	C17—O10	1.220 (5)
C3—O4	1.362 (6)	C17—O12	1.350 (6)
C4—N1	1.292 (6)	C18—N3	1.313 (6)
C4—H4A	0.9300	C18—H18A	0.9300
C5—O4	1.447 (5)	C19—O12	1.439 (5)
C5—H5C	0.9600	C19—H19C	0.9600
C5—H5B	0.9600	C19—H19B	0.9600
C5—H5A	0.9600	C19—H19A	0.9600
C6—O3	1.435 (5)	C20—O11	1.452 (5)
C6—H6C	0.9600	C20—H20C	0.9600
C6—H6B	0.9600	C20—H20B	0.9600
C6—H6A	0.9600	C20—H20A	0.9600
C7—N1	1.465 (6)	C21—N3	1.467 (6)
C7—H7C	0.9600	C21—H21C	0.9600
C7—H7B	0.9600	C21—H21B	0.9600
C7—H7A	0.9600	C21—H21A	0.9600
N1—H1	0.8600	N3—H3	0.8600
C8—O5	1.228 (5)	C22—O13	1.207 (5)
C8—O7	1.326 (6)	C22—O15	1.338 (5)
C8—C9	1.466 (6)	C22—C23	1.459 (6)
C9—C11	1.383 (6)	C23—C25	1.388 (7)
C9—C10	1.450 (6)	C23—C24	1.443 (7)
C10—O6	1.228 (5)	C24—O14	1.235 (5)
C10—O8	1.324 (5)	C24—O16	1.335 (6)
C11—N2	1.305 (6)	C25—N4	1.302 (6)
C11—H11A	0.9300	C25—H25A	0.9300
C12—O8	1.438 (5)	C26—O16	1.444 (5)
C12—H12C	0.9600	C26—H26C	0.9600
C12—H12B	0.9600	C26—H26B	0.9600
C12—H12A	0.9600	C26—H26A	0.9600
C13—O7	1.440 (5)	C27—O15	1.465 (5)
C13—H13C	0.9600	C27—H27C	0.9600
C13—H13B	0.9600	C27—H27B	0.9600
C13—H13A	0.9600	C27—H27A	0.9600

supplementary materials

C14—N2	1.449 (6)	C28—N4	1.460 (6)
C14—H14C	0.9600	C28—H28C	0.9600
C14—H14B	0.9600	C28—H28B	0.9600
C14—H14A	0.9600	C28—H28A	0.9600
N2—H2	0.8600	N4—H4	0.8600
O1—C1—O3	121.1 (4)	O9—C15—O11	120.7 (4)
O1—C1—C2	124.2 (5)	O9—C15—C16	123.5 (5)
O3—C1—C2	114.7 (4)	O11—C15—C16	115.8 (4)
C4—C2—C3	113.4 (5)	C18—C16—C17	112.7 (4)
C4—C2—C1	117.9 (5)	C18—C16—C15	119.9 (4)
C3—C2—C1	128.7 (5)	C17—C16—C15	127.4 (5)
O2—C3—O4	120.0 (5)	O10—C17—O12	119.6 (4)
O2—C3—C2	124.8 (5)	O10—C17—C16	124.3 (5)
O4—C3—C2	115.2 (4)	O12—C17—C16	116.1 (4)
N1—C4—C2	129.8 (5)	N3—C18—C16	126.8 (4)
N1—C4—H4A	115.1	N3—C18—H18A	116.6
C2—C4—H4A	115.1	C16—C18—H18A	116.6
O4—C5—H5C	109.5	O12—C19—H19C	109.5
O4—C5—H5B	109.5	O12—C19—H19B	109.5
H5C—C5—H5B	109.5	H19C—C19—H19B	109.5
O4—C5—H5A	109.5	O12—C19—H19A	109.5
H5C—C5—H5A	109.5	H19C—C19—H19A	109.5
H5B—C5—H5A	109.5	H19B—C19—H19A	109.5
O3—C6—H6C	109.5	O11—C20—H20C	109.5
O3—C6—H6B	109.5	O11—C20—H20B	109.5
H6C—C6—H6B	109.5	H20C—C20—H20B	109.5
O3—C6—H6A	109.5	O11—C20—H20A	109.5
H6C—C6—H6A	109.5	H20C—C20—H20A	109.5
H6B—C6—H6A	109.5	H20B—C20—H20A	109.5
N1—C7—H7C	109.5	N3—C21—H21C	109.5
N1—C7—H7B	109.5	N3—C21—H21B	109.5
H7C—C7—H7B	109.5	H21C—C21—H21B	109.5
N1—C7—H7A	109.5	N3—C21—H21A	109.5
H7C—C7—H7A	109.5	H21C—C21—H21A	109.5
H7B—C7—H7A	109.5	H21B—C21—H21A	109.5
C1—O3—C6	115.1 (4)	C15—O11—C20	115.3 (4)
C3—O4—C5	115.6 (4)	C17—O12—C19	115.9 (4)
C4—N1—C7	123.2 (4)	C18—N3—C21	122.5 (4)
C4—N1—H1	118.4	C18—N3—H3	118.7
C7—N1—H1	118.4	C21—N3—H3	118.7
O5—C8—O7	123.5 (4)	O13—C22—O15	122.7 (4)
O5—C8—C9	120.8 (5)	O13—C22—C23	123.1 (5)
O7—C8—C9	115.7 (4)	O15—C22—C23	114.2 (4)
C11—C9—C10	113.6 (4)	C25—C23—C24	113.1 (5)
C11—C9—C8	119.4 (5)	C25—C23—C22	119.3 (5)
C10—C9—C8	127.0 (4)	C24—C23—C22	127.6 (5)
O6—C10—O8	119.7 (5)	O14—C24—O16	119.8 (4)
O6—C10—C9	124.2 (5)	O14—C24—C23	124.0 (5)
O8—C10—C9	116.1 (4)	O16—C24—C23	116.2 (4)

N2—C11—C9	129.5 (4)	N4—C25—C23	128.4 (5)
N2—C11—H11A	115.3	N4—C25—H25A	115.8
C9—C11—H11A	115.3	C23—C25—H25A	115.8
O8—C12—H12C	109.5	O16—C26—H26C	109.5
O8—C12—H12B	109.5	O16—C26—H26B	109.5
H12C—C12—H12B	109.5	H26C—C26—H26B	109.5
O8—C12—H12A	109.5	O16—C26—H26A	109.5
H12C—C12—H12A	109.5	H26C—C26—H26A	109.5
H12B—C12—H12A	109.5	H26B—C26—H26A	109.5
O7—C13—H13C	109.5	O15—C27—H27C	109.5
O7—C13—H13B	109.5	O15—C27—H27B	109.5
H13C—C13—H13B	109.5	H27C—C27—H27B	109.5
O7—C13—H13A	109.5	O15—C27—H27A	109.5
H13C—C13—H13A	109.5	H27C—C27—H27A	109.5
H13B—C13—H13A	109.5	H27B—C27—H27A	109.5
N2—C14—H14C	109.5	N4—C28—H28C	109.5
N2—C14—H14B	109.5	N4—C28—H28B	109.5
H14C—C14—H14B	109.5	H28C—C28—H28B	109.5
N2—C14—H14A	109.5	N4—C28—H28A	109.5
H14C—C14—H14A	109.5	H28C—C28—H28A	109.5
H14B—C14—H14A	109.5	H28B—C28—H28A	109.5
C8—O7—C13	114.7 (4)	C22—O15—C27	114.7 (4)
C10—O8—C12	116.1 (4)	C24—O16—C26	115.3 (4)
C11—N2—C14	123.4 (4)	C25—N4—C28	122.9 (4)
C11—N2—H2	118.3	C25—N4—H4	118.6
C14—N2—H2	118.3	C28—N4—H4	118.6
O1—C1—C2—C4	0.8 (8)	O9—C15—C16—C18	-5.1 (8)
O3—C1—C2—C4	-178.1 (5)	O11—C15—C16—C18	176.0 (5)
O1—C1—C2—C3	-178.7 (5)	O9—C15—C16—C17	175.9 (6)
O3—C1—C2—C3	2.4 (8)	O11—C15—C16—C17	-3.0 (7)
C4—C2—C3—O2	5.5 (8)	C18—C16—C17—O10	2.3 (8)
C1—C2—C3—O2	-175.0 (5)	C15—C16—C17—O10	-178.6 (5)
C4—C2—C3—O4	-176.0 (5)	C18—C16—C17—O12	-177.3 (4)
C1—C2—C3—O4	3.5 (8)	C15—C16—C17—O12	1.8 (8)
C3—C2—C4—N1	-179.8 (5)	C17—C16—C18—N3	177.3 (5)
C1—C2—C4—N1	0.6 (9)	C15—C16—C18—N3	-1.9 (8)
O1—C1—O3—C6	-1.6 (7)	O9—C15—O11—C20	1.4 (7)
C2—C1—O3—C6	177.3 (4)	C16—C15—O11—C20	-179.7 (4)
O2—C3—O4—C5	0.4 (7)	O10—C17—O12—C19	2.6 (7)
C2—C3—O4—C5	-178.1 (4)	C16—C17—O12—C19	-177.8 (4)
C2—C4—N1—C7	178.8 (5)	C16—C18—N3—C21	-176.1 (5)
O5—C8—C9—C11	-8.2 (7)	O13—C22—C23—C25	1.8 (8)
O7—C8—C9—C11	173.8 (5)	O15—C22—C23—C25	-175.5 (5)
O5—C8—C9—C10	173.2 (5)	O13—C22—C23—C24	-178.0 (5)
O7—C8—C9—C10	-4.7 (7)	O15—C22—C23—C24	4.8 (8)
C11—C9—C10—O6	-0.6 (8)	C25—C23—C24—O14	5.0 (8)
C8—C9—C10—O6	178.0 (5)	C22—C23—C24—O14	-175.2 (5)
C11—C9—C10—O8	178.8 (4)	C25—C23—C24—O16	-174.8 (4)
C8—C9—C10—O8	-2.6 (8)	C22—C23—C24—O16	4.9 (8)

supplementary materials

C10—C9—C11—N2	-179.9 (5)	C24—C23—C25—N4	179.9 (5)
C8—C9—C11—N2	1.3 (8)	C22—C23—C25—N4	0.1 (9)
O5—C8—O7—C13	2.5 (7)	O13—C22—O15—C27	1.1 (7)
C9—C8—O7—C13	-179.6 (4)	C23—C22—O15—C27	178.3 (4)
O6—C10—O8—C12	-0.3 (7)	O14—C24—O16—C26	-0.1 (7)
C9—C10—O8—C12	-179.8 (4)	C23—C24—O16—C26	179.8 (4)
C9—C11—N2—C14	-175.4 (5)	C23—C25—N4—C28	-179.7 (5)

Hydrogen-bond geometry (Å, °)

<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	0.86	2.08	2.689 (4)	127
N1—H1 \cdots O10	0.86	2.42	2.990 (4)	125
N2—H2 \cdots O5	0.86	2.08	2.687 (4)	127
N2—H2 \cdots O14 ⁱ	0.86	2.30	2.893 (5)	127
N3—H3 \cdots O9	0.86	2.06	2.684 (4)	129
N3—H3 \cdots O2 ⁱ	0.86	2.32	2.912 (5)	126
N4—H4 \cdots O13	0.86	2.08	2.698 (5)	128
N4—H4 \cdots O6	0.86	2.40	2.957 (5)	123
C4—H4A \cdots O2	0.93	2.27	2.683 (7)	106
C6—H6A \cdots O14	0.96	2.50	3.449 (7)	169
C11—H11A \cdots O6	0.93	2.29	2.706 (6)	107
C11—H11A \cdots O13	0.93	2.60	3.487 (6)	159
C14—H14A \cdots O13	0.96	2.59	3.507 (6)	161
C18—H18A \cdots O1	0.93	2.58	3.470 (6)	160
C18—H18A \cdots O10	0.93	2.27	2.679 (6)	106
C25—H25A \cdots O14	0.93	2.28	2.691 (6)	106
C27—H27A \cdots O2 ⁱ	0.96	2.59	3.340 (7)	135
C28—H28C \cdots O6	0.96	2.60	3.024 (6)	107

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

Fig. 1

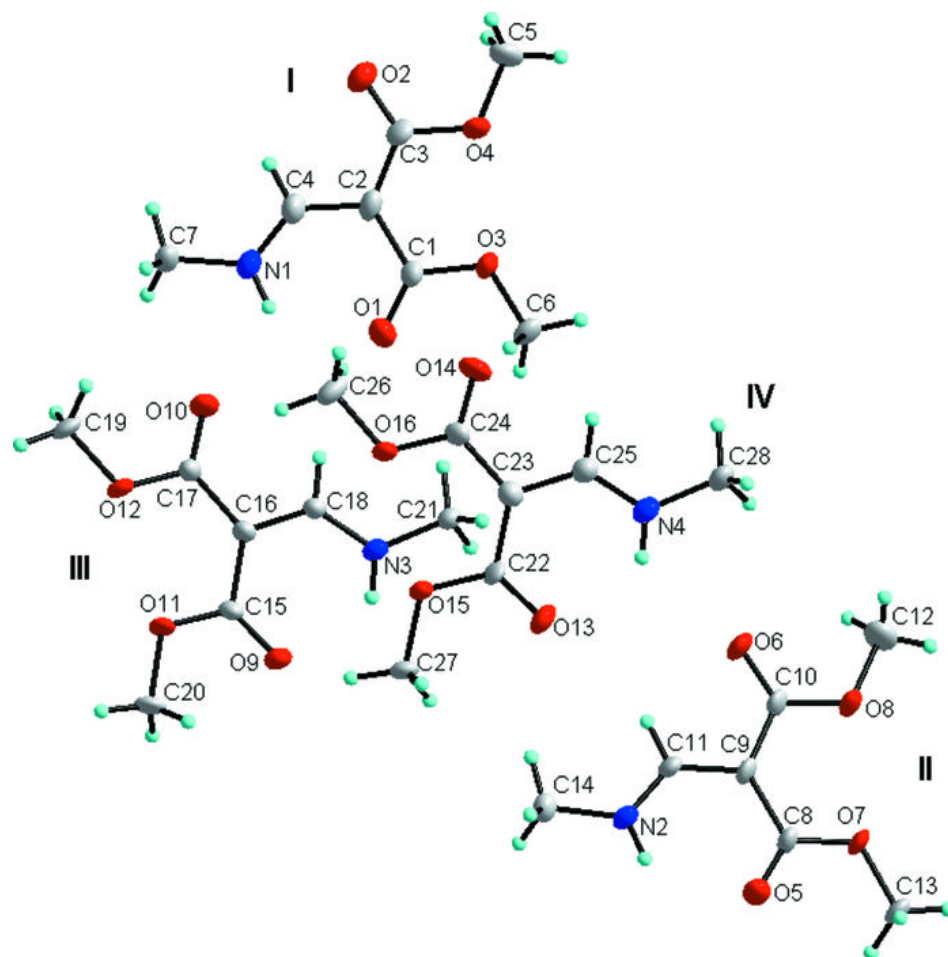


Fig. 2

