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Diethyl 2-(4-nitrophenyl)malonate forms a hydrogen-bonded chain of rings

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Molecules of the title compound, $C_{13}H_{15}NO_6$, are linked by two C—H···O hydrogen bonds [H···O = 2.32 and 2.46 Å, C···O = 3.306 (2) and 3.393 (2) Å, and C—H···O = 171 and 156°] into a $C(4)C(7)[R_3^2(11)]$ chain of rings.

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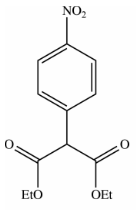
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.125
Data-to-parameter ratio = 17.1

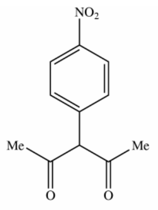
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

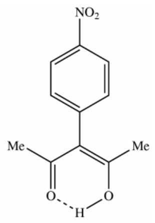
Molecules of the title compound, (I) (Fig. 1), are linked by two C—H···O hydrogen bonds (Table 1) to form a chain of rings. The tertiary atom C7 lies between two carboxylate groups and thus carries one of the more acidic C—H bonds in the molecule; atom C7 in the molecule at (x, y, z) acts as hydrogen-bond donor to carboxylate atom O92 in the molecule at (x, $\frac{3}{2} - y, \frac{1}{2} + z$), while C7 at ($x, \frac{3}{2} - y, \frac{1}{2} + z$) in turn acts as donor to O92 at (x, y, 1+z). In this manner a $C(4)$ chain is produced, running parallel to the [001] direction and generated by the c-glide plane at y = 0.75. This chain is reinforced by a second, weaker C—H···O hydrogen bond. Atom C81 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* H81B, to O92 in the molecule at (x, y, 1 + z), so generating by translation a $C(7)$ chain parallel to [001]. The combination of these two motifs thus generates a $C(4)C(7)[R_3^2(11)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to [001] (Fig. 2). There are two chains of this type, related to one another by inversion, running through each unit cell, but there are no direction-specific interactions between adjacent chains. In particular, there are no C—H···π(arene) hydrogen bonds nor any aromatic π–π stacking interactions in the structure.



(I)



(II)



(IIa)

It is noteworthy that a single atom, O92, acts as acceptor in both hydrogen bonds, whereas none of the other O atoms participates in the hydrogen bonding, and that both of the hydrogen-bond donors are aliphatic C atoms. Neither the aryl C—H bonds nor the nitro O atoms participate in any way in the supramolecular aggregation. The bond lengths and interbond angles in (I) show no unusual values.

Closely related to (I) is the diketone (II), which was found (Emsley *et al.*, 1989) to exist in the solid state solely as the enol (IIa), stabilized by a short intramolecular O—H···O hydrogen bond. The intermolecular interactions were not

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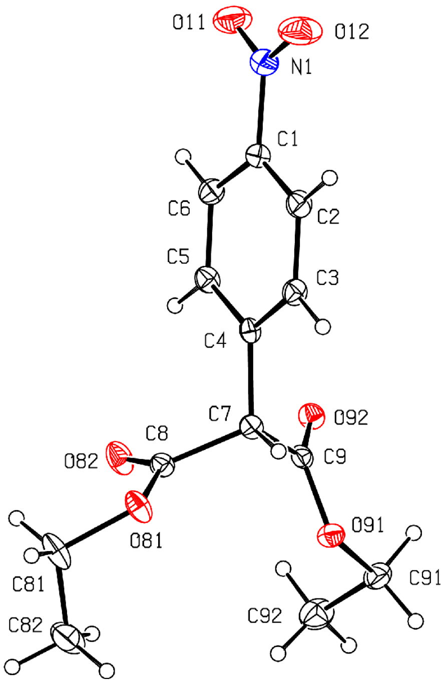

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

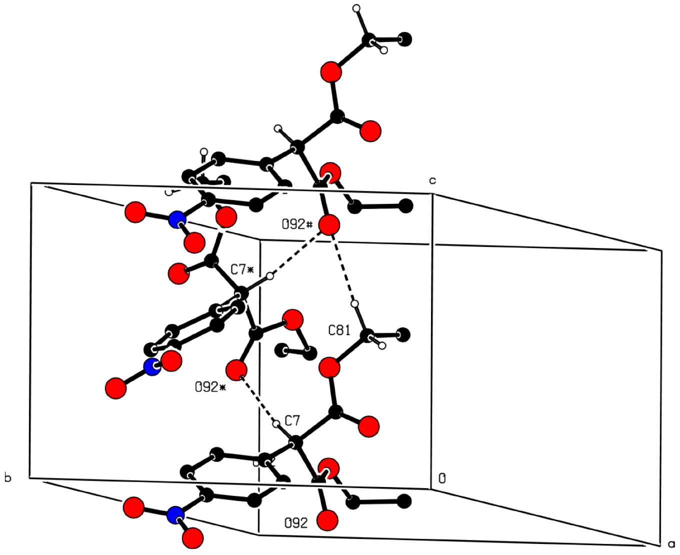

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of rings along [001]. For the sake of clarity, H atoms bonded to the C atoms which do not participate in the motifs shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions (x, $\frac{3}{2} - y$, $\frac{1}{2} + z$) and (x, y, $1 + z$), respectively.

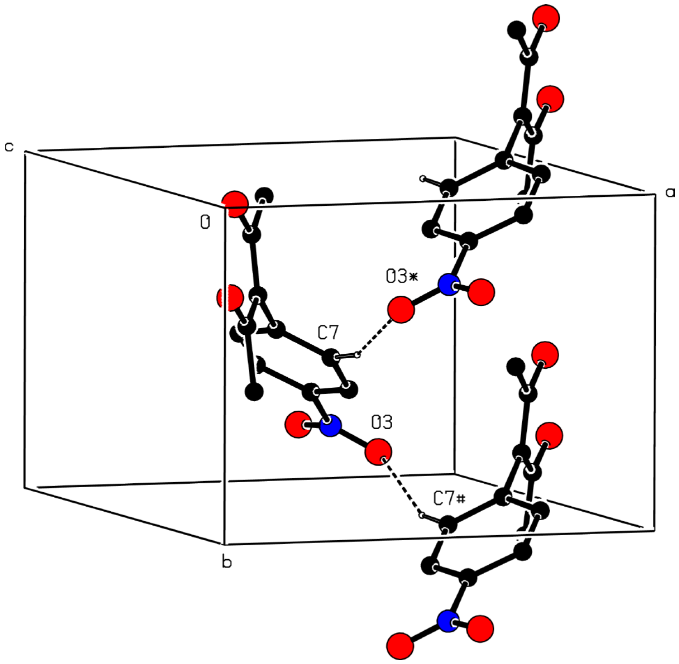

Figure 3
Part of the crystal structure of (II), showing the formation of a $C(6)$ chain along [010]; the atomic coordinates and the atom labels are as given in the original report (Emsley *et al.*, 1989). For the sake of clarity, H atoms which do not participate in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) and ($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$), respectively.

discussed in the original report, but scrutiny of the atomic coordinates retrieved from the Cambridge Structural Database (Allen, 2002), refcode SAPYEN, shows that the molecules are linked by a single C—H···O hydrogen bond into $C(6)$ chains generated by the 2_1 screw axes in space group $P2_1/c$ (Fig. 3). We note here that the hydrogen-bond donor in (II) is one of the aryl C atoms, whereas in (I) the aryl C atoms play no role in the supramolecular aggregation. Likewise, the hydrogen-bond acceptor in (II) is one of the nitro O atoms (Fig. 3), while the nitro group in (I) plays no role in the supramolecular aggregation.

Experimental

A sample of compound (I) was prepared by the CuBr-catalysed coupling reaction in dioxane solution between 4-nitrobromobenzene and the monosodium salt of diethylmalonate, Na[CH(COOEt)$_2$], following the general procedure described by Setsune *et al.* (1981). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol, and had a melting point of 330–332 K.

Crystal data

$C_{13}H_{15}NO_6$
$M_r = 281.26$
Monoclinic, $P2_1/c$
$a = 11.9275$ (6) Å
$b = 13.8407$ (8) Å
$c = 8.4595$ (3) Å
$\beta = 99.192$ (3)°
$V = 1378.60$ (12) Å^3
$Z = 4$
$D_x = 1.355$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3150 reflections
$\theta = 2.9$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.35 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.967$, $T_{\max} = 0.991$
14 747 measured reflections
3150 independent reflections
2007 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 15$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.125$
$S = 1.00$
3150 reflections
184 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.0884P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O92^{i}	1.00	2.32	3.306 (2)	171
C81—H81B···O92^{ii}	0.99	2.46	3.393 (2)	156

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

All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic CH), and with U_{iso}(H) = $1.2U_{eq}$(C) (CH and CH_2) or $1.5U_{eq}$(C) (CH_3).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Emsley, J., Ma, L. Y. Y., Bates, P. A., Motevalli, M. & Hursthouse, M. B. (1989). *J. Chem. Soc. Perkin Trans* 2, pp. 527–533.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version, Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Setsune, J., Matsukawa, K., Wakemoto, H. & Kitao, T. (1981). *Chem. Lett.* **36**, 367–370.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.