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Supramolecular structures of 5-[3-(4-methylphenyl)- and 5-[3-(4-chlorophenyl)-2-propenylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione

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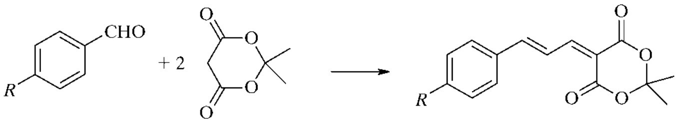
2,2-Dimethyl-5-[3-(4-methylphenyl)-2-propenylidene]-1,3-dioxane-4,6-dione, $C_{16}H_{16}O_4$, crystallizes in the triclinic space group $P\overline{1}$, with two molecules in the asymmetric unit. These molecules and a centrosymmetrically related pair, linked together by weak C—H···O hydrogen bonds, form a tetramer. 5-[3-(4-Chlorophenyl)-2-propenylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione, $C_{15}H_{13}ClO_4$, also crystallizes in the triclinic space group $P\overline{1}$, with one molecule in the asymmetric unit. Centrosymmetrically related molecules are linked together by weak C—H···O hydrogen bonds to form dimers which are further linked by yet another pair of centrosymmetrically related C—H···O hydrogen bonds to form a tube which runs parallel to the *a* axis.

Comment

Meldrum's acid and its derivatives serve as good synthetic equivalents, most often in the preparation of arylidene condensation products, which have received little attention as intermediates in heterocyclic synthesis. The condensations of arylidene derivatives of Meldrum's acid with heterocyclic monoamines to afford pyridines (Morales *et al.*, 1996; Quiroga *et al.*, 1997, 1998, 1999; Rodríguez *et al.*, 1996, 1997) or with α,β-unsaturated or dicarbonyl compounds to afford coumarins (Margaretha, 1972) have been reported.

We report here an attempt to prepare triazolopyrimidine or triazolopyridazine using such a condensation reaction involving Meldrum's acid, 1,2-diaminotriazole and benzaldehyde. The final product was surprisingly the 3-phenyl-2-propenylidene derivative of Meldrum's acid, which comes from condensation of two molecules of Meldrum's acid with one of benzaldehyde. A further reaction using only the Meldrum's acid and benzaldehyde also produced that compound.

Both of the title compounds crystallize in space group $P\overline{1}$, in the case of compound (3*a*), with two molecules in the asymmetric unit, which was chosen such that it formed a centrosymmetric dimer (see below). Views of molecules *A* and *B* of (3*a*) are shown in Figs. 1(*a*) and 1(*b*), respectively. A view of molecule (3*b*) is shown in Fig. 2. The numbering system has been chosen to be consistent for all three molecules.



(1*a*): *R* = Me
(1*b*): *R* = Cl
(2)
(3*a*): *R* = Me
(3*b*): *R* = Cl

The bonds and angles for the three molecules discussed in this study show no major differences except for the torsion angles involving the junction of the phenyl group and the propylidene chain. These difference are probably related to the differences in supramolecular structures found for the compounds. Selected torsion angles are given in Tables 1 and 3 for (3*a*) and (3*b*), respectively.

The supramolecular structures of each compound are different. In compound (3*a*), the two molecules (*A* and *B*) in the asymmetric unit are linked together head-to-tail *via*

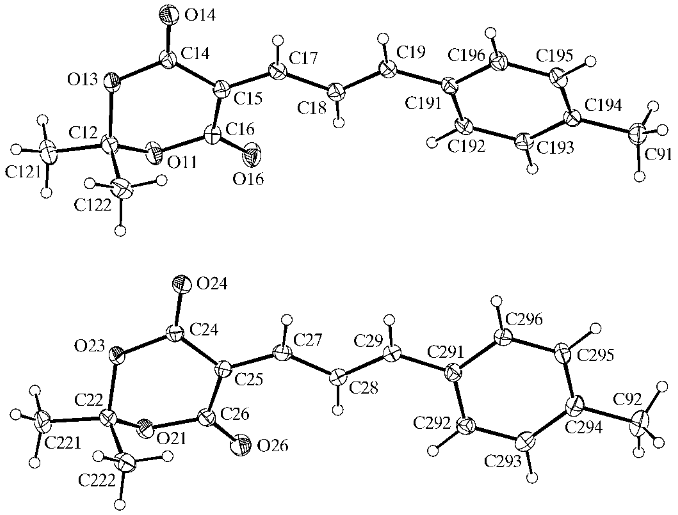


Figure 1
A view of (*a*) molecule *A* and (*b*) molecule *B* of compound (3*a*). Displacement ellipsoids are drawn at the 30% probability level.

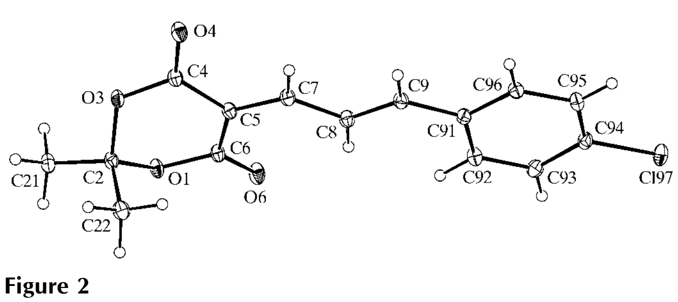


Figure 2
A view of compound (3*b*) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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C193—H193···O21 and C293—H293···O11 weak hydrogen bonds to form a dimer comprising an $R_2^2(20)$ ring (Bernstein *et al.*, 1995). These dimers are further linked together by two centrosymmetrically related pairs of weak C—H···O hydrogen bonds in which O24 at $(-x, 1 - y, 2 - z)$ is an acceptor for H29 and H296, thus forming an $R_2^1(6)$ ring, (Bernstein *et al.*, 1995). Hence, a discrete tetramer is formed by the molecules in the asymmetric unit dimer and the dimer related to it by a centre of symmetry at $(0, \frac{1}{2}, 1)$ (Fig. 3).

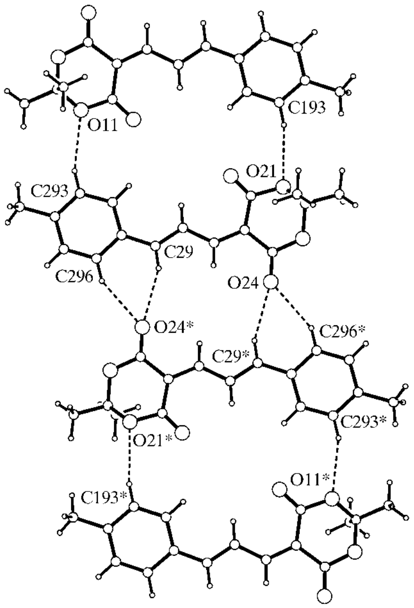

Figure 3
A view of the discrete tetramer formed by the molecules of (3*a*). The atoms labelled with an asterisk (*) are at $(-x, 1 - y, 2 - z)$. The unit cell has been omitted for the sake of clarity.

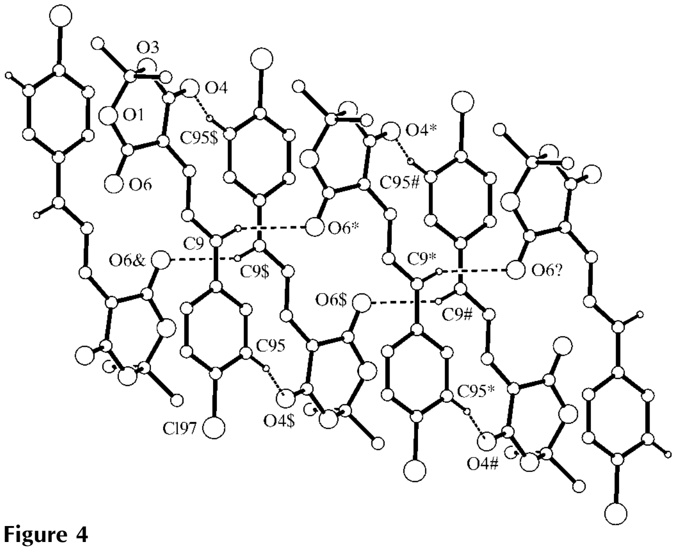

Figure 4
A view of (3*b*) showing the $R_2^2(20)$ dimers and *C*(7) chains and the $R_4^4(28)$ ring. The unit cell has been omitted for the sake of clarity. The atoms labelled with an asterisk (*), hash (#), dollar sign ($), question mark (?) or ampersand (&) are at $(x - 1, y, z)$, $(-x, 2 - y, 2 - z)$, $(1 - x, 2 - y, 2 - z)$, $(x - 2, y, z)$ and $(2 - x, 2 - y, 2 - z)$, respectively.

In compound (3*b*), in which there is only one molecule in the centrosymmetric unit, the C95—H95···O4$(1 - x, 2 - y, 2 - z)$ weak hydrogen bond links the molecules into a centrosymmetric dimer centred on $(\frac{1}{2}, 1, 1)$, giving an $R_2^2(20)$ ring (Bernstein *et al.*, 1995). In addition the molecules are linked by the C9—H9···O6$(x - 1, y, z)$ weak hydrogen bond to form a *C*(7) chain running parallel to the *a* axis. Operation of the centre of symmetry at (0, 1, 1) produces an $R_4^4(28)$ ring (Bernstein *et al.*, 1995), resulting from a combination of centrosymmetrically related pairs of C95—H95···O4 and C9—H9···O6 hydrogen bonds (Fig. 4). The result is a tube-like three-dimensional ribbon which runs parallel to the *a* axis.

There is also a short Cl97···Cl97$(1 - x, 1 - y, 3 - z)$ contact of 3.4927 (8) Å in (3*b*). A preliminary search of the Cambridge Structural Database (Allen & Kennard, 1993) gave 1544 hits for short Cl···Cl contacts less than the van der Waals contact distance of 3.6 Å for Cl attached to C atoms.

Experimental

For the preparation of 2,2-dimethyl-5-[3-(4-methylphenyl)-2-propenylidene]-1,3-dioxane-4,6-dione, (3*a*), a solution of 4-methylbenzaldehyde, (1*a*) (2.0 mmol), and Meldrum's acid, (2) (4.0 mmol), in ethoxyethanol (5 ml) with catalytic amounts of triethylamine was refluxed for 30 min [with thin-layer chromatography (TLC) control]. The resulting precipitate was filtered off, washed with ethanol, dried and purified by silica-gel chromatography with chloroform. Orange crystals of (3*a*) suitable for X-ray diffraction were prepared by diffusion using ethyl acetate and hexane (m.p. 401 K, yield 65%). For the preparation of 5-[3-(4-chlorophenyl)-2-propenylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione, (3*b*), a solution of 4-chlorobenzaldehyde, (1*b*) (2.0 mmol), and Meldrum's acid, (2) (4.0 mmol), in ethoxyethanol (5 ml) with catalytic amounts of triethylamine was refluxed for 30 min (with TLC control). Orange crystals of (3*b*) (m.p. 455 K, yield 70%) were obtained as for (3*a*).

Compound (3*a*)

Crystal data

$C_{16}H_{16}O_4$
$M_r = 272.29$
Triclinic, $P\overline{1}$
$a = 11.2891$ (3) Å
$b = 11.4128$ (4) Å
$c = 13.4504$ (5) Å
$\alpha = 91.217$ (2)°
$\beta = 114.640$ (3)°
$\gamma = 113.7590$ (15)°
$V = 1403.88$ (8) Å^3

$Z = 4$
$D_x = 1.288$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6331 reflections
$\theta = 2.9$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 120$ (1) K
Lath, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.991$, $T_{\max} = 0.999$
21 945 measured reflections

6331 independent reflections
3359 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.080$
$\theta_{\max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.165$
$S = 0.96$
6331 reflections
367 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Table 1
Selected torsion angles (°) for (3*a*).

C14—C15—C17—C18	−178.75 (19)	C24—C25—C27—C28	−178.17 (19)
C16—C15—C17—C18	−2.3 (4)	C26—C25—C27—C28	−1.7 (3)
C15—C17—C18—C19	−179.8 (2)	C25—C27—C28—C29	−179.7 (2)
C17—C18—C19—C191	−179.61 (19)	C27—C28—C29—C291	178.55 (19)
C18—C19—C191—C192	5.4 (3)	C28—C29—C291—C292	−8.7 (3)
C18—C19—C191—C196	−174.6 (2)	C28—C29—C291—C296	171.8 (2)

Table 2
Hydrogen-bonding geometry (Å, °) for (3*a*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C29—H29···O24^{i}	0.95	2.52	3.412 (3)	156
C193—H193···O21	0.95	2.60	3.531 (3)	166
C296—H296···O24^{i}	0.95	2.56	3.425 (3)	152
C293—H293···O11	0.95	2.54	3.422 (3)	154

Symmetry code: (i) $-x, 1-y, 2-z$.

Compound (3b)

Crystal data

$C_{15}H_{13}ClO_4$
$M_r = 292.70$
Triclinic, $P\bar{1}$
$a = 7.2648$ (2) Å
$b = 7.4705$ (3) Å
$c = 13.5855$ (6) Å
$\alpha = 90.1799$ (13)°
$\beta = 99.8452$ (14)°
$\gamma = 109.576$ (3)°
$V = 683.01$ (4) Å^3

$Z = 2$
$D_x = 1.423$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3057 reflections
$\theta = 3.0$–27.5°
$\mu = 0.29$ mm^{-1}
$T = 120$ (1) K
Block, yellow
0.15 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.958$, $T_{max} = 0.972$
9407 measured reflections

3057 independent reflections
2350 reflections with $I > 2\sigma(I)$
$R_{int} = 0.077$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.153$
$S = 0.98$
3057 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0932P)^2 + 0.2802P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 3
Selected torsion angles (°) for (3*b*).

C4—C5—C7—C8	−174.20 (19)	C7—C8—C9—C91	−176.20 (19)
C6—C5—C7—C8	1.9 (4)	C8—C9—C91—C92	−3.5 (3)
C5—C7—C8—C9	179.3 (2)	C8—C9—C91—C96	175.4 (2)

Molecules (3*a*) and (3*b*) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H = 0.95–0.98 Å. Methyl-H atoms were calculated as six half H atoms at the corners of a regular hexagon. Examination of the structure with *PLATON* (Spek, 2001) showed that there were no solvent-accessible voids in the crystal lattice.

Table 4
Hydrogen-bonding geometry (Å, °) for (3*b*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O6^{i}	0.95	2.53	3.380 (3)	149
C95—H95···O4^{ii}	0.95	2.56	3.396 (3)	146

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, 2-y, 2-z$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997) and *KappaCCD Server Software*; data reduction: *DENZO-SMN* and *KappaCCD Server Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997) program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1522). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Johnson, C. K. (1976). *ORTEP*II. Technical Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Margaretha, P. (1972). *Angew. Chem.* **84**, 308–311.

Morales, A., Ochoa, E., Suárez, M., Verdecia, Y., González, L., Martín, N., Quinteiro, M., Seoane, C. & Soto, J. L. (1996). *J. Heterocycl. Chem.* **33**, 103–108.

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 & R. M. Sweet, pp. 307–326. London: Academic Press.

Quiroga, J., Hormaza, A., Insuasty, B. & Márquez, M. (1998). *J. Heterocycl. Chem.* **35**, 409–412.

Quiroga, J., Hormaza, A., Insuasty, B., Nogueras, M., Sánchez, A., Hanold, N. & Meier, H. (1997). *J. Heterocycl. Chem.* **34**, 521–524.

Quiroga, J., Insuasty, B., Hormaza, A., Cabildo, P., Claramunt, R. M. & Elguero, J. (1999). *Heterocycl. Commun.* **5**, 115–122.

Rodríguez, R., Suárez, M., Ochoa, E., Morales, A., González, L., Martín, N., Quinteiro, M., Seoane, C. & Soto, J. L. (1996). *J. Heterocycl. Chem.* **33**, 45–48.

Rodríguez, R., Suárez, M., Ochoa, E., Morales, A., González, L., Martín, N., Quinteiro, M., Seoane, C. & Soto, J. L. (1997). *J. Heterocycl. Chem.* **34**, 957–960.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2001). *PLATON.* Version of October 2001. University of Utrecht, The Netherlands.