Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.260 (5)	C1—C2	1.520 (5)
O2—C1	1.236 (5)	C2—C5	1.526 (6)
N1—C2	1.480 (5)	C3—C4	1.494 (7)
N1—C3	1.504 (6)	C4—C5	1.510 (6)
C2—N1—C3	107.8 (3)	N1—C2—C5	104.7 (3)
O2—C1—O1	125.9 (4)	C1—C2—C5	113.2 (3)
O2—C1—C2	117.8 (4)	C4—C3—N1	101.4 (3)
O1—C1—C2	116.4 (3)	C3—C4—C5	103.7 (3)
N1—C2—C1	111.4 (3)	C4—C5—C2	105.5 (4)
C3—N1—C2—C1	106.7 (3)	C2—N1—C3—C4	35.7 (4)
C3—N1—C2—C5	−16.1 (4)	N1—C3—C4—C5	−40.8 (4)
O2—C1—C2—N1	179.3 (3)	C3—C4—C5—C2	32.0 (4)
O1—C1—C2—N1	−1.9 (4)	N1—C2—C5—C4	−9.8 (4)
O2—C1—C2—C5	−63.0 (5)	C1—C2—C5—C4	−131.4 (3)
O1—C1—C2—C5	115.8 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O1^{i}	0.900	1.841	2.723 (4)	165.7 (2)
N1—H1···O1	0.900	2.153	2.632 (4)	112.5 (2)
O3—H311···O2	0.996	1.833	2.815 (4)	168.3 (2)
O3—H312···O3^{ii}	0.886	2.158	2.889 (5)	139.4 (3)
O3—H313···O3^{iii}	0.902	2.035	2.902 (6)	160.7 (2)
N1—H1···O3^{iv}	0.900	2.581	3.243 (5)	130.9 (2)

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

All H atoms were located in difference Fourier maps and were not refined.

Data collection: Stoe AED diffractometer software. Cell refinement: Stoe AED diffractometer software. Data reduction: Stoe AED diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1239). Services for accessing these data are described at the back of the journal.

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An Extended Imide Containing Two Methylene Meldrum's Acid Units

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Abstract

We report the crystal structure of the unusual imide 5,5′-(iminodimethylidene)bis(2,2-dimethyl-1,3-dioxane-4,6-dione), $C_{14}H_{15}NO_8$, which contains two Meldrum's acid (dioxanedione) substituents. The geometry of the imide moiety shows the effects of delocalization of the N-atom

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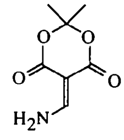
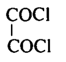
lone pair, while the overall conformation of the molecule is associated with the formation of strong intramolecular hydrogen bonds.

Comment

As a continuation of our work on the reactions of aminomethylene Meldrum's acid, (1), with acid chlorides (McNab & Withell, 1996), we investigated its reaction with oxalyl chloride, (2). Surprisingly, the only significant product after 20 h under reflux in MeCN was the extended imide (3) (18%), and we now report the characterization of this compound by X-ray crystallography.

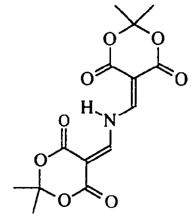


(1)



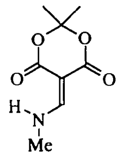
$\mathrm{COCl}-\mathrm{COCl}$

(2)

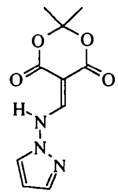


(3)

Compound (3) shows an *sE* configuration about both N1—C7 and N1—C7′, allowing intramolecular bifurcated hydrogen bonding of N1—H with O6 and O6′. Delocalization of the N1 lone pair through two methylenedioxanedione systems is reflected in the much longer N1—C7/7′ bond lengths [average 1.362 (8) Å] compared with those of the aminomethylenedioxanedione model compounds (4) (Blake, Hunter & McNab, 1989) [1.281 (14) Å] and (5) (Blake, Gould, Irving, McNab & Morrow, 1994) [1.315 (2) Å]. The average C5/5′—C7/7′ distance [1.350 (9) Å] in (3) shows correspondingly more double-bond character than in both (4) [1.409 (15) Å] and (5) [1.373 (2) Å], but the effect is much smaller and less significant. The average C4/4′—C5/5′ bond length [1.465 (9) Å] is slightly longer than the average C5/5′—C6/6′ bond length [1.451 (9) Å], and although this distinction is of borderline significance in (3), a similar consistent effect is seen in the model compounds (4) and (5), which may be taken to imply a resonance contribution to the hydrogen bonding in these systems. The average C6/6′—C5/5′—C7/7′ bond angle [121.6 (7)°] is larger than C4/4′—C5/5′—C7/7′ [117.3 (7)°] in order to accommodate the hydrogen bond. In general, the bond angles in (3) are very similar to those in (4) and (5).



(4)



(5)

The conformations of the dioxanedione rings in (3) can both be described as being approximately 30% chair and 70% boat (Gould, Taylor & Thorpe, 1995). With the exception of the atoms C2 and C2′ and their methyl substituents, the molecule is essentially planar, with the largest deviation from the mean plane being that of O4′ (0.211 Å).

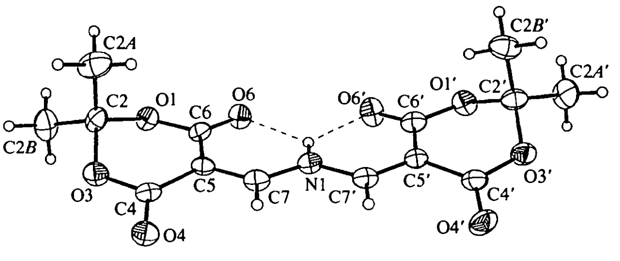
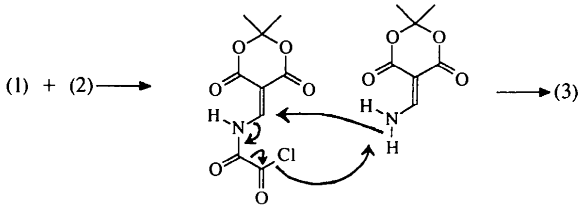


Fig. 1. A view of the molecule with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces. H atoms have been assigned arbitrary radii.

The reasons for the unexpected formation of (3) remain unclear, but it may be significant that much longer reaction times are required than for related reactions (McNab & Withell, 1996). The oxalyl chloride plays a significant role in the process since if (1) is heated for 20 h in MeCN in the presence of triethylamine and in the absence of oxalyl chloride, the starting material (1) is quantitatively recovered. The mechanism shown in the scheme below is consistent with these observations.



Experimental

A solution of oxalyl chloride (1.26 g, 10 mmol) in acetonitrile (10 ml) was added dropwise to a stirred solution of (1) (1.71 g, 10 mmol) and triethylamine (2.04 g, 20 mmol) in acetonitrile (40 ml) over a period of 10 min. The mixture was heated under reflux for 20 h and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (100 ml) and extracted with water (2 × 100 ml). A further portion of water (100 ml) was added and the gelatinous mixture was filtered through celite. The organic layer was separated, washed with dilute hydrochloric acid (1 *M*, 50 ml) and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give (3) (0.30 g, 18%), m.p. 501 K (dec.) (from acetonitrile). Elemental analysis found C 51.4, H 5.05, N 4.25%; $C_{14}H_{15}NO_8$ requires C 51.7, H 4.55, N 4.3%. NMR: δ_H ($CDCl_3$) 12.80 (1H, *t*, ^3J = 12.6 Hz), 8.84 (2H, *d*, ^3J = 12.6 Hz) and 1.70 p.p.m. (12H, *s*); δ_C ($CDCl_3$) 162.65 (*q*), 161.34 (*q*), 156.33, 105.66 (*q*), 96.40 (*q*) and 26.95 p.p.m. *m/z*

(EI): 325 (M^+, 19%), 268 (12), 267 (75), 210 (22), 209 (42), 181 (20), 165 (20), 153 (63), 137 (28) and 121 (47).

Crystal data

$C_{14}H_{15}NO_8$
$M_r = 325.27$
Triclinic
$P\bar{1}$
$a = 5.191\ (4)$ Å
$b = 11.627\ (6)$ Å
$c = 12.998\ (7)$ Å
$\alpha = 75.80\ (4)°$
$\beta = 79.33\ (6)°$
$\gamma = 88.49\ (6)°$
$V = 747.2\ (8)$ Å^3
$Z = 2$
$D_x = 1.446$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 9.5–12.0°$
$\mu = 0.120$ mm^{-1}
$T = 298\ (2)$ K
Lath
0.31 × 0.12 × 0.04 mm
Pale yellow

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
2607 measured reflections
1954 independent reflections
734 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.188$

$\theta_{\rm max} = 22.5°$
$h = -5 \rightarrow 5$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 13$
3 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.113$
$S = 0.980$
1946 reflections
209 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$

$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0091 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

O1—C6	1.354 (7)	O1′—C6′	1.361 (8)
O1—C2	1.442 (7)	O1′—C2′	1.438 (8)
C2—O3	1.455 (8)	C2′—O3′	1.433 (8)
O3—C4	1.357 (7)	O3′—C4′	1.359 (8)
C4—O4	1.202 (7)	C4′—O4′	1.209 (8)
C4—C5	1.466 (9)	C4′—C5′	1.463 (9)
C5—C7	1.352 (9)	C5′—C7′	1.347 (9)
C5—C6	1.447 (8)	C5′—C6′	1.454 (9)
C6—O6	1.209 (7)	C6′—O6′	1.211 (8)
C7—N1	1.351 (8)	N1—C7′	1.373 (8)
O6···O6′	3.178 (7)		

The crystal diffracted only weakly at higher angles and accordingly data were collected to only $2\theta_{\rm max} = 45°$, resulting in a low data-to-parameter ratio. The high value of $R_{\rm int}$ reflects the distribution of equivalents over rather weak high-angle data.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1995).

We thank EPSRC for provision of a four-circle diffractometer and postgraduate funding for KW, and Lonza Ltd for a gift of Meldrum's acid.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1340). Services for accessing these data are described at the back of the journal.

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1,3-Di(ethoxy-ethoxy-methoxy)calix[4]-arene†

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Abstract

In the solid state, the title compound, $C_{38}H_{44}O_8$, adopts a cone conformation, which is somewhat distorted. The cone conformation is also observed by NMR spectroscopy in solution. The distortion consists of a

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† Alternative name: 26,28-bis(3,6-dioxaheptyloxy)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,-19(26),21,23-dodecaene-25,27-diol.