Newkome, G. R., Moorefield, C. N., Baker, G. R., Johnson, A. L. & Behera, R. K. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1176–1178.

Newkome, G. R., Nayak, A., Behera, R. J., Moorefield, C. N. & Baker, G. R. (1992). *J. Org. Chem.* **57**, 358–362.

Structure of a Hexasubstituted 1,3-Dioxane Compound Derived from Meldrum's Acid: $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$

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Abstract

The species $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$ (diethyl 2,2-dimethyl-4,6-dioxo-1,3-dioxane-5,5-diacetate) was synthesized from Meldrum's acid and ethyl bromoacetate and subjected to an X-ray diffraction study. The molecule has approximate C_{2v} symmetry. The 1,3-dioxane system is essentially planar and has neither the boat nor the chair conformation typical of saturated six-membered 1,3-dioxane rings.

Comment

'Meldrum's acid', $C_6H_8O_4$, was first reported more than 80 years ago as the product of the condensation of malonic acid with acetone. It was originally misformulated (Meldrum, 1908) as the carboxylic acid $C(O)$—O—CMe_2—$CHCO_2H$. This product was correctly identified as isopropylidene malonate or 2,2-dimethyl-1,3-dioxane-4,6-dione by Davidson & Bernhard (1948). This compound has been used extensively as an organic reagent (Fieser & Fieser, 1967; McNab, 1978). Most 1,3-dioxane derivatives have a boat conformation, although 2,2,5,5-tetrasubstituted compounds favor the chair conformation (Jones & Kennard, 1977). In contrast to this, the present structure is based upon a planar (± 0.007 Å) hexasubstituted 1,3-dioxane ring. Deviations of atoms from the least-squares plane of the 1,3-dioxane ring are -0.003 for C(1), -0.007 for C(12), 0.014 for O(13), -0.012 for C(14), 0.003 for O(15) and 0.005 Å for C(16). The two O atoms linked by C=O

double bonds [C(12)—O(12) = 1.197 (3) and C(16)—O(16) = 1.199 (3) Å] to the ring are also essentially coplanar with the dioxane ring with deviations of -0.039 for O(12) and 0.014 Å for O(16). The remaining substituents are located symmetrically above and below the 1,3-dioxane plane with deviations of -1.276 for C(17), 1.215 for C(18), -1.235 for C(22) and 1.221 Å for C(32).
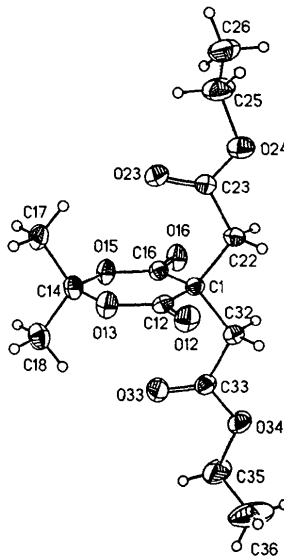

Fig. 1. Labelling of atoms in $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$; *ORTEP*II (Johnson, 1976) diagram with 50% probability ellipsoids and H atoms artificially reduced.

Experimental

Crystal data

$C_{14}H_{20}O_8$	$D_x = 1.315$ Mg m^{-3}
$M_r = 316.3$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71073$ Å
$P2_1/c$	Cell parameters from 50
$a = 17.696$ (4) Å	reflections
$b = 10.360$ (2) Å	$\theta = 12.5–15.0°$
$c = 8.733$ (1) Å	$\mu = 0.102$ mm^{-1}
$\beta = 93.47$ (2)°	$T = 295$ K
$V = 1598.0$ (5) Å^3	Plate
$Z = 4$	$0.6 \times 0.5 \times 0.3$ mm
	Colorless

Data collection

Siemens *R3m/V* diffractometer	$\theta_{max} = 22.5°$
	$h = -19 \rightarrow 19$
2θ(counter)–θ(crystal) scans	$k = -11 \rightarrow 0$
Absorption correction:	$l = -9 \rightarrow 9$
none	3 standard reflections
4488 measured reflections	monitored every 97
2103 independent reflections	reflections
2103 observed reflections	intensity variation: not
[$F > 0.5\sigma(F)$]	significant
$R_{int} = 0.0127$	

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Refinement

Refinement on F	$w = [\sigma^2(F)+0.0005F^2]^{-1}$
Final $R = 0.0651$	$(\Delta/\sigma)_{max} = 0.002$
(0.0422 for $F > 6\sigma$)	
$wR = 0.0621$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
(0.0564 for $F > 6\sigma$)	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$S = 1.60$	Atomic scattering factors
2103 reflections	from *International Tables*
220 parameters	*for X-ray Crystallography*
Only H-atom U's refined	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	0.2411 (1)	0.9589 (2)	−0.1024 (3)	0.049 (1)
C(12)	0.2141 (1)	1.0855 (3)	−0.0396 (3)	0.051 (1)
O(12)	0.1843 (1)	1.1658 (2)	−0.1213 (2)	0.079 (1)
O(13)	0.2223 (1)	1.1102 (2)	0.1084 (2)	0.069 (1)
C(14)	0.2530 (2)	1.0245 (3)	0.2260 (3)	0.061 (1)
O(15)	0.2792 (1)	0.9041 (2)	0.1649 (2)	0.064 (1)
C(16)	0.2754 (1)	0.8688 (3)	0.0196 (3)	0.053 (1)
O(16)	0.2997 (1)	0.7648 (2)	−0.0117 (2)	0.076 (1)
C(17)	0.1917 (2)	0.9945 (3)	0.3317 (3)	0.074 (1)
C(18)	0.3196 (2)	1.0899 (3)	0.3060 (4)	0.084 (1)
C(22)	0.1738 (1)	0.8922 (3)	−0.1918 (3)	0.058 (1)
C(23)	0.1093 (2)	0.8622 (3)	−0.0973 (4)	0.066 (1)
O(23)	0.1126 (1)	0.8590 (3)	0.0389 (3)	0.126 (1)
O(24)	0.0472 (1)	0.8379 (2)	−0.1810 (3)	0.093 (1)
C(25)	−0.0211 (2)	0.7990 (5)	−0.1050 (6)	0.109 (2)
C(26)	−0.0254 (3)	0.6625 (5)	−0.0919 (7)	0.128 (2)
C(32)	0.2992 (1)	0.9858 (3)	−0.2248 (3)	0.062 (1)
C(33)	0.3722 (2)	1.0430 (3)	−0.1642 (4)	0.063 (1)
O(33)	0.3867 (1)	1.0690 (3)	−0.0322 (3)	0.097 (1)
O(34)	0.4181 (1)	1.0632 (3)	−0.2730 (2)	0.090 (1)
C(35)	0.4927 (2)	1.1177 (7)	−0.2280 (5)	0.133 (2)
C(36)	0.5211 (3)	1.1825 (7)	−0.3452 (8)	0.202 (4)

Table 2. *Geometric parameters* (Å, °)

C(1)—C(12)	1.510 (4)	C(1)—C(16)	1.515 (3)
C(1)—C(22)	1.547 (3)	C(1)—C(32)	1.553 (4)
C(12)—O(12)	1.197 (3)	C(12)—O(13)	1.317 (3)
O(13)—C(14)	1.439 (3)	C(14)—O(15)	1.444 (3)
C(14)—C(17)	1.500 (4)	C(14)—C(18)	1.495 (4)
O(15)—C(16)	1.318 (3)	C(16)—O(16)	1.199 (3)
C(22)—C(23)	1.481 (4)	C(23)—O(23)	1.187 (4)
C(23)—O(24)	1.307 (4)	O(24)—C(25)	1.469 (5)
C(25)—C(26)	1.420 (7)	C(32)—C(33)	1.489 (4)
C(33)—O(33)	1.196 (4)	C(33)—O(34)	1.304 (4)
O(34)—C(35)	1.466 (5)	C(35)—C(36)	1.346 (9)
C(12)—C(1)—C(16)	113.7 (2)	C(12)—C(1)—C(22)	108.7 (2)
C(16)—C(1)—C(22)	110.1 (2)	C(12)—C(1)—C(32)	109.3 (2)
C(16)—C(1)—C(32)	109.9 (2)	C(22)—C(1)—C(32)	104.8 (2)
C(1)—C(12)—O(12)	121.6 (2)	C(1)—C(12)—O(13)	120.5 (2)
O(12)—C(12)—O(13)	117.9 (2)	C(12)—O(13)—C(14)	126.5 (2)
O(13)—C(14)—O(15)	112.7 (2)	O(13)—C(14)—C(17)	108.1 (2)
O(15)—C(14)—C(17)	108.0 (2)	O(13)—C(14)—C(18)	107.9 (2)
O(15)—C(14)—C(18)	107.6 (2)	C(17)—C(14)—C(18)	112.6 (2)
C(14)—O(15)—C(16)	126.6 (2)	C(1)—C(16)—O(15)	120.1 (2)
C(1)—C(16)—O(16)	121.9 (2)	O(15)—C(16)—O(16)	118.1 (2)
C(1)—C(22)—C(23)	114.1 (2)	C(22)—C(23)—O(23)	124.8 (3)
C(22)—C(23)—O(24)	112.3 (3)	O(23)—C(23)—O(24)	122.9 (3)
C(23)—O(24)—C(25)	119.2 (3)	O(24)—C(25)—C(26)	111.1 (4)
C(1)—C(32)—C(33)	115.1 (2)	C(32)—C(33)—O(33)	124.3 (3)
C(32)—C(33)—O(34)	111.7 (2)	O(33)—C(33)—O(34)	124.0 (3)
C(33)—O(34)—C(35)	117.2 (3)	O(34)—C(35)—C(36)	111.1 (4)

The title compound was synthesized in the following manner. A solution of ethylbromoacetate (34 g, 0.2 mol) in 50 ml of acetonitrile was added to a 150 ml round-bottomed flask containing Meldrum's acid (14.5 g, 0.1 mol). The mixture was stirred for a few minutes at room temperature to obtain a uniform solution and then ground K_2CO_3 powder (13.8 g) was introduced. The resulting solution was stirred under gentle reflux for 12 h. Most of the acetonitrile was removed by rotary evaporation at 323–333 K and about 100 ml of ice water was poured into the residue and agitated. A large amount of white crystalline product precipitated out. Well formed crystals were grown from a 3:2:1 mixed solvent of chloroform, petroleum ether and ether under refrigeration.

The data were corrected for Lorentz and polarization effects but not for absorption. Empirical ψ scans were collected and as their transmission factors were in the range 0.97–0.98, it was concluded that the statistical counting errors in these ψ scans would outweigh the effect of any applied 'absorption corrections'. Axial photographs indicated that the crystal belonged to the monoclinic system ($2/m$ Laue symmetry). The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely define the space group $P2_1/c$ [C_{2h}^5; No. 14].

All crystallographic calculations were performed on a VAX 3100 workstation using *SHELXTL-Plus* (Sheldrick, 1990). The analytical scattering factors for the neutral atoms were corrected for the real and imaginary components of anomalous dispersion. The structure was solved by a combination of direct methods and difference Fourier synthesis. H atoms were included in idealized positions based on C—H = 0.96 Å (Churchill, 1973), but their individual isotropic thermal parameters were refined.

References

Churchill, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.
Davidson, D. & Bernhard, S. A. (1948). *J. Am. Chem. Soc.* **70**, 3426–3428.
Fieser, L. F. & Fieser, M. (1967). *Reagents for Organic Synthesis*, pp. 526–527. New York: John Wiley.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jones, P. G. & Kennard, O. (1977). *Cryst. Struct. Commun.* **6**, 97–101.
McNab, H. (1978). *Chem. Soc. Rev.* **7**, 345–358.
Meldrum, A. N. (1908). *J. Chem. Soc.* **93**, 598–601.
Sheldrick, G. M. (1990). *SHELXTL-Plus.* Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.