Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 864-866

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.12965

Synthesis and Crystal Structure of 5-(4-Methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione

WULAN ZENG

MicroScale Science Institute, Department of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

Corresponding author: Fax: +86 536 8785802; Tel: +86 536 8785802; E-mail: wulanzeng@163.com

(*Received*: 31 October 2011; *Accepted*: 22 August 2012) AJC-11997

A new Meldrum's acid compound 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione was prepared by 2,2-dimethyl-1,3-dioxane-4,6-dione with 4-methoxybenzaldehyde in ethanol and its crystal structure was determined by X-ray crystallographic techniques. It crystallizes in triclinic, space group P-1 with a = 9.1249(6) Å, b = 9.9060(8) Å, c = 14.4640(16) Å, α = 85.1440(10)º, β = 84.7750(10)º, γ = 89.388(2)º, $C_{14}H_{14}O_5$, Mr = 262.25, V = 1297.3(2) Å^3, Z = 4, D_c = 1.343 g/cm^3, $F_{(000)}$ = 552, μ = 0.102 mm^{-1}. The 1,3-dioxane ring is in a distorted envelope conformation. The crystal structure is stabilized by weak intermolecular C-H···O hydrogen bonds.

Key Words: Synthesis, Crystal structure, 2,2-Dimethyl-1,3-dioxane-4,6-dione, Meldrum's acid.

INTRODUCTION

Considerable interest has been focused on the Meldrum's acid owing to its susceptibility to nucleophilic attack and to electophilic attack, extensive experimental efforts have been made to seek the compounds containing Meldrum's acid fragment[1-6]. On the other hand, Meldrum's acid and its derivatives have been widely used in fine chemical and pharmaceutical industry. Therefore, it is important to design and synthesize a new Meldrum's acid compound. The compound 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**I**) was synthesized by the uncatalyzed reaction of 2,2-dimethyl-1,3-dioxane-4,6-dione and 4-methoxybenzaldehyde in ethanol. In order to confirm its structure, single crystals of 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione were obtained by evaporation of petroleum ether-ethylacetate (4:1) solution of (**I**) at room temperature over a period of several days and the molecular structure was determined by X-ray diffraction.

EXPERIMENTAL

All the reagents and solvents from commercial sources were used without further purification. Elemental analyses were obtained using an American Perkin Elmer 2400 analyzer. IR spectra (4000-400 cm^{-1}), were recorded on a Nicolet FT-IR 510P spectrometer. Melting points were measured by using a melting point apparatus made in Shanghai Instrument Limited Company.

A mixture of 4-methoxybenzaldehyde (1.36 g, 0.01 mol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (1.44 g, 0.01 mol) was stirred in ethanol (20 mL) for 2 h at reflux temperature. After cooling to room temperature, the precipitate was filtered off and dried. Yield 48 %. m.p. 121.0-122.5 ºC. Anal. calcd. (%) for $C_{14}H_{14}O_5$: C, 67.53; H, 4.80, found: C, 68.74; H, 5.17. The single crystal suitable for X-ray diffraction analysis was obtained by evaporation for petroleum ether and ethyl acetate (4:1 = v/v) after a few days.

Data collection and structure determination: A selected crystal of the title compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 293 K, using a graphite monochromator MoK$_\alpha$ (λ = 0.071073 nm) radiation with an ω scan mode. A total of 6740 reflections were collected and 4495 were independent (R_{int} = 0.0281) in the range of 2.40 < θ < 25.02º, of which 2561 reflections were observed with I > 2σ(I).

The structure of the title compound was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package[7]. All non-hydrogen atoms were refined by full-matrix least-squares method, while all hydrogen atoms were placed in the geometrically calculated positions. The contributions of these hydrogen atoms were included in the structure-factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography[8]. The crystal and experimental data are shown in Table-1.

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione are given in Table-2 and

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	$C_{14}H_{14}O_5$
Formula weight	262.25
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.1249(6) Å α = 85.1440(10)°
	b = 9.9060(8) Å β = 84.7750(10)°
	c = 14.4640(16) Å γ = 89.388(2)°
Volume (Å^3), Z	1297.3(2),4
Calculated density (g/cm^3)	1.343
Absorption coefficient (mm^{-1})	0.102
$F_{(000)}$	552
Crystal size (mm)	0.50 mm × 0.40 mm × 0.39 mm
Theta range for Data collection (°)	2.40-25.02
Limiting indices	-10 ⇐ h ⇐ 10, -6 ⇐ k ⇐ 11, -17 ⇐ l ⇐ 17
Reflections collected/unique	6740/4495 [$R_{(int)}$ = 0.0281]
Completeness to theta = 25.02	98.4 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4495/0/350
Goodness-of-fit on F^2	1.012
Final R indices [I > 2σ(I)]	R1 = 0.0444, wR2 = 0.0977
R indices (all data)	R1 = 0.0916, wR2 = 0.1223
Largest diff. peak and hole (Einstein Å^{-3})	0.145 and -0.163

the selected bond distances and bond angles in Table-3. A displacement ellipsoid plot with atomic numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell in Fig. 2.

The crystal lattices of 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione comprise two symmetry-independent molecule in the unit cell. Each symmetry-independent molecule consists of 1,3-dioxane ring and 4-methoxypheneyl ring. The corresponding bond lengths and angles for the independent molecules agree well with each other. The bond lengths of C(2)-C(7) and C(16)-C(21)

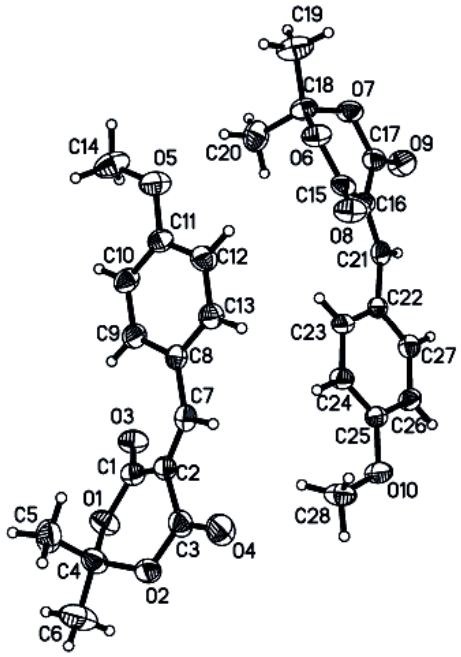

Fig. 1. Molecular structure with atomic numbering scheme

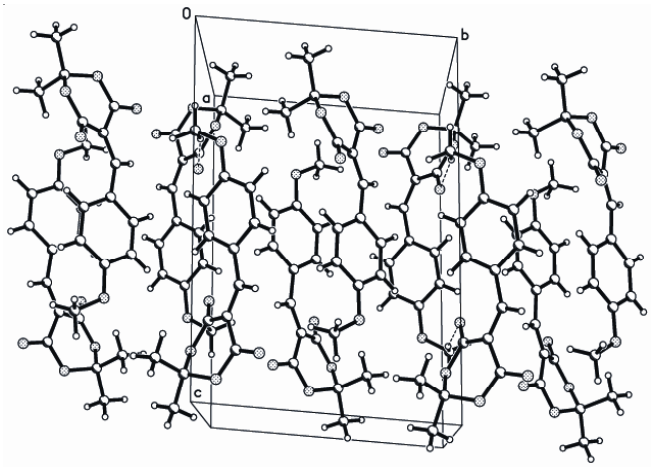

Fig. 2. View of crystal packing

TABLE-2
ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (Å^2 × 10^3)

Atom	x	y	Z	U(eq)	Atom	x	y	Z	U(eq)
O(1)	3497(2)	-324(2)	8405(1)	67(1)	C(10)	2290(3)	230(3)	4502(2)	62(1)
O(2)	1621(2)	813(2)	9238(1)	64(1)	C(11)	1495(3)	1069(3)	3929(2)	54(1)
O(3)	4224(2)	317(2)	6952(1)	65(1)	C(12)	670(3)	2110(3)	4300(2)	64(1)
O(4)	409(3)	2504(2)	8584(1)	89(1)	C(13)	648(3)	2285(3)	5223(2)	59(1)
O(5)	1413(2)	934(2)	3011(1)	75(1)	C(14)	2213(3)	-147(4)	2606(2)	86(1)
O(6)	1813(2)	4793(2)	11908(1)	60(1)	C(15)	2095(3)	5441(3)	12652(2)	50(1)
O(7)	3865(2)	5716(2)	10999(1)	64(1)	C(16)	3552(3)	6046(2)	12633(2)	45(1)
O(8)	1099(2)	5541(2)	13251(1)	67(1)	C(17)	4352(3)	6349(3)	11706(2)	56(1)
O(9)	5348(2)	7137(2)	11523(1)	80(1)	C(18)	2984(3)	4531(3)	11218(2)	59(1)
O(10)	3060(2)	6286(2)	17237(1)	64(1)	C(19)	2252(4)	4301(4)	10360(2)	93(1)
C(1)	3275(3)	364(3)	7583(2)	53(1)	C(20)	3903(3)	3358(3)	11560(2)	83(1)
C(2)	1928(3)	1189(2)	7567(2)	49(1)	C(21)	4173(3)	6479(2)	13365(2)	49(1)
C(3)	1246(3)	1576(3)	8479(2)	61(1)	C(22)	3808(3)	6356(2)	14367(2)	43(1)
C(4)	2288(3)	-478(3)	9114(2)	64(1)	C(23)	2817(3)	5446(2)	14849(2)	50(1)
C(5)	1177(4)	-1458(3)	8859(2)	86(1)	C(24)	2541(3)	5389(3)	15802(2)	49(1)
C(6)	2948(4)	-896(4)	10004(2)	104(1)	C(25)	3264(3)	6258(2)	16297(2)	47(1)
C(7)	1290(3)	1684(2)	6804(2)	52(1)	C(26)	4280(3)	7167(3)	15838(2)	53(1)
C(8)	1451(3)	1457(2)	5824(2)	47(1)	C(27)	4555(3)	7194(2)	14893(2)	52(1)
C(9)	2272(3)	427(3)	5426(2)	61(1)	C(28)	2094(3)	5307(3)	17738(2)	76(1)

TABLE-4
INTERMOLECULAR INTERACTION DISTANCES (Å)

D-H-A	Symmetry	D-H	H···A	D···A	D-H···A
C(14)-H(14A)···O(3)	1-x, -y, 1-z	0.9600	2.4398	3.370(3)	163.09
C(7)-H(7)···O(4)	–	0.9295	2.3902	2.811(3)	107.33
C(9)-H(9)···O(3)	–	0.9297	2.2649	2.954(3)	130.45
C(21)-H(21)···O(9)	–	0.9298	2.3893	2.805(3)	106.96
C(23)-H(23)···O(8)	–	0.9299	2.2856	2.904(3)	123.52

TABLE-3
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Bond	Å	Bond	Å
C(7)-C(8)	1.449(3)	C(21)-C(22)	1.452(3)
C(2)-C(7)	1.348(3)	C(16)-C(21)	1.347(3)
O(1)-C(1)	1.350(3)	O(5)-C(11)	1.354(3)
O(1)-C(4)	1.436(3)	O(5)-C(14)	1.427(3)
O(3)-C(1)	1.204(3)	O(6)-C(15)	1.344(3)
O(4)-C(3)	1.200(3)	O(6)-C(18)	1.432(3)
O(5)-C(11)	1.354(3)	O(7)-C(17)	1.354(3)
O(5)-C(14)	1.427(3)	O(7)-C(18)	1.427(3)
O(2)-C(3)	1.347(3)	O(10)-C(25)	1.358(3)
O(2)-C(4)	1.428(3)	O(10)-C(28)	1.424(3)
Angles	(º)	Angles	(º)
C(2)-C(7)-C(8)	135.6(2)	C(16)-C(21)-C(22)	134.6(2)
C(9)-C(8)-C(7)	125.8(2)	C(23)-C(22)-C(21)	125.6(2)
C(13)-C(8)-C(7)	117.8(2)	C(27)-C(22)-C(21)	117.4(2)

[1.348(3) and 1.347(3) Å] confirm the localization of the double bond at this position and are consistent with those of the related structure reported earlier[8,9]. The C(7)-C(8) and C(21)-C(22) distances of 1.449(3), 1.452(3) Å in molecules, respectively, are in good agree with the values reported in the literature[10]. The 1,3-dioxane rings of the two molecules have the same almost identical distorted envelope conformations.

In the crystal structure lattice of the title compound, the molecules form a three dimensional net work through hydrogen bonds. Five hydrogen bonds of C-H···O are divided into two types, one intermolecular hydrogen bond and four intramolecular hydrogen bonds. The hydrogen bond lengths and bond angles are listed in Table-4. In solid state, all above hydrogen bonds stabilize the crystal structure.

ACKNOWLEDGEMENTS

This project supported by the Natural Science Foundation of Shandong Province (No. ZR2010CL011) and (No. ZR2010BM033).

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