Asian Journal of Chemistry; Vol. 26, No. 14 (2014), 4359-4362

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16509

Synthesis and Crystal Structure of 2,2-Dimethyl-5-((2-phenylhydrazinyl)methylene)-1,3-dioxane-4,6-dione

WU-LAN ZENG[1,*] and HUI-LIAN LIU[2]

[1]Microscale Science Institute, Department of Chemistry, Chemical Engineering and Environmental Engineering, Weifang University, Weifang 261061, P.R. China
[2]Microscale Science Institute, College of Bioengineering, Weifang University, Weifang 261061, Shandong Province, P.R. China

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

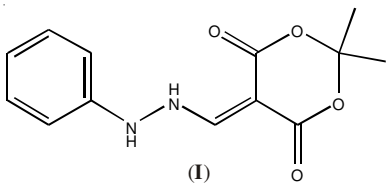
Received: 10 October 2013; *Accepted*: 18 March 2014; *Published online*: 5 July 2014; AJC-15475

A new Meldrum's acid compound 2,2-dimethyl-5-((2-phenylhydrazinyl)methylene)-1,3-dioxane-4,6-dione was prepared by 2,2-dimethyl-1,3-dioxane-4,6-dione, methylorthoformate and phenylhydrazine in ethanol and its crystal structure was determined by X-ray crystallographic techniques. It crystallizes in Triclinic, space group P-1 with a = 13.514 (3) Å, b = 13.550 (3) Å, c = 13.599 (3) Å, α = 104.01 (3)°, β = 103.90 (3)°, γ = 103.91 (3)°, $C_{13}H_{14}N_2O_4$, Mr = 262.26, V = 2224.4 (11) Å^3, Z = 6, Dc = 1.175 g/cm^3, F (000) = 828, μ = 0.088 mm^{-1}. The 1,3-dioxane ring is in a screw-boat conformation. The crystal structure is stabilized by weak intermolecular C–H···O and N–H···O.

Keywords: 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[1-4]. 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. For these reasons, our group have developed a new simple strategy towards the construction of various Meldrum's acid compounds[5-8]. The title compound 2,2-dimethyl-5-((2-phenylhydrazinyl)methylene)-1,3-dioxane-4,6-dione (**I**) was synthesized by uncatalyzed reaction of 2,2-dimethyl-1,3-dioxane-4,6-dione, methylorthoformate and phenylhydrazine in ethanol. In order to confirm its structure, single crystals of the title compound were obtained by evaporation of petroleum ether-ethyl acetate (3:1) solution of (**I**) at room temperature over a period of several days and the molecular structure was determined by X-ray diffraction.



(I)

EXPERIMENTAL

All the reagents and solvents from commercial sources were used without further purification. Melting points were measured by using a melting point apparatus made in Shanghai Instrument Limited Company. X-ray diffraction was performed on a SMART CCD area detector diffractometer.

A mixture of methylorthoformate (1.27 g, 0.012 mol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (1.44 g, 0.01 mol) was stirred in ethanol (30 mL) for 2 h at reflux temperature. Then the phenylhydrazine (1.08 g, 0.01 mol) was added into the solution. The mixture was heated under reflux for another 6 h. After cooling to room temperature, the precipitate was filtered off and dried. Yield 27.2 %. m.p.: 132.2-134.1 °C.

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 14579 reflections were collected and 7759 were independent (Rint = 0.0487) in the range of $3.14 < \theta < 27.33°$, of which 3498 reflections were observed with $I > 2\sigma$ (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[9]. 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[10]. 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 the title compound are given in Table-2 and 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.

In the title compound, the bond lengths and angles in the phenyl ring are generally normal. As can be seen from the crystal structure (Fig. 1), the crystal lattices of 2,2-dimethyl-5-((2-phenylhydrazinyl)methylene)-1,3-dioxane-4,6-dione comprise three symmetry-independent molecules in the unit cell. Each symmetry-independent molecule consists of 1,3-dioxane ring and 2-phenylhydrazine ring. The corresponding bond lengths and angles for the independent molecules agree well with each other. The bond lengths of C(7A)-C(9A), C(7B)-C(9B) and C(7C)-C(9C) [1.398 (5), 1.402 (5) and 1.395 (5) Å] confirm the localization of the double bond at this position. The bond lengths of N (2A)-C (7A) (1.302 (5), Å), N (2B)-C (7B) (1.298 (5), Å) and N (2C)-C (7C) (1.311 (4), Å) are all similar to those of the standard C-N single bond length. The 1,3-dioxane rings of the three molecules have the same screw-boat conformations.

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

Empirical formula	$C_{13}H_{14}N_2O_2$
Formula weight	262.26
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	a = 13.514(3) Å α = 104.01(3) ° b = 13.550(3) Å β = 103.90(3) ° c = 13.599(3) Å γ = 103.91(3) °
Volume(Å^3), Z	2224.3(8),6
Calculated density (g/cm^3)	1.176
Absorption coefficient (mm^{-1})	1.176
F (000)	828
Crystal size (mm)	0.36 × 0.28 × 0.18 mm
Theta range for data collection (°)	3.14-27.88
Limiting indices	-17 <=h <= 17, -17 <= k <= 17, -17 <= l <= 14
Reflections collected/unique	14579/7759 [R(int) = 0.0487]
Completeness to θ = 27.33	77.0 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7759/0/514
Goodness-of-fit on F^2	1.202
Final R indices [I > 2σ (I)]	R_1 = 0.0981, wR_2 = 0.2591
R indices (all data)	R_1 = 0.1342, wR_2 = 0.2724
Largest diff. peak and hole (Einstein Å^{-3})	0.826 and -0.289

In the crystal structure lattice of the title compound, the molecules form a three dimensional net work through hydrogen bonds. There are six intramolecular hydrogen bonds and pack-

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(4C)	6883(2)	1715(3)	1165(2)	59(1)	O(1C)	7537(2)	2471(3)	2941(2)	68(1)
O(4B)	3843(2)	3117(2)	3290(3)	61(1)	N(2B)	1108(2)	291(3)	1849(3)	43(1)
O(2C)	9718(2)	1510(2)	873(2)	54(1)	N(1B)	262(3)	-693(3)	1334(3)	50(1)
O(3C)	7994(2)	1289(2)	119(2)	55(1)	N(2C)	9709(3)	3151(3)	3888(2)	43(1)
O(2B)	2060(2)	2465(2)	2536(3)	66(1)	C(9C)	8783(3)	2232(3)	2012(3)	41(1)
O(3B)	4883(2)	2008(2)	3715(2)	56(1)	N(1C)	10685(3)	3668(3)	4737(3)	49(1)
O(1B)	4127(2)	278(3)	3492(2)	55(1)	C(7B)	2075(3)	305(3)	2306(3)	42(1)
C(9B)	2989(3)	1217(3)	2768(3)	40(1)	C(7C)	9693(3)	2687(3)	2916(3)	42(1)
C(8B)	3991(3)	1097(4)	3316(3)	43(1)	C(8C)	8904(3)	1681(3)	1005(3)	44(1)
C(1C)	10674(3)	3505(4)	5728(3)	48(1)	C(13C)	7392(5)	2845(5)	74(4)	84(2)
C(10B)	2899(3)	2258(4)	2823(4)	50(1)	C(4B)	-2690(5)	-690(6)	1833(6)	106(2)
C(1B)	-731(3)	-672(3)	1497(3)	49(1)	C(3B)	-1767(5)	-139(5)	2625(5)	81(2)
C(6C)	10121(4)	2510(4)	5789(4)	56(1)	C(5C)	10135(5)	2372(5)	6764(4)	79(2)
C(11B)	4839(3)	2887(4)	3295(4)	57(1)	C(13B)	4933(4)	2605(5)	2154(4)	82(2)
C(11C)	7115(4)	1706(4)	162(3)	58(1)	C(12B)	5739(4)	3858(4)	4104(5)	92(2)
C(10C)	7735(3)	2178(4)	2103(3)	50(1)	C(3C)	11232(7)	4151(6)	7656(4)	115(3)
C(2B)	-792(4)	-114(4)	2482(4)	59(1)	C(4C)	10684(6)	3157(6)	7683(5)	107(2)
C(6B)	-1682(4)	-1242(5)	670(4)	81(2)	C(5B)	-2662(4)	-1237(6)	853(6)	112(3)
C(12C)	6138(4)	909(5)	-733(4)	92(2)	O(4A)	1719(3)	6158(2)	1883(2)	61(1)
N(1A)	3668(3)	9741(3)	5689(3)	48(1)	O(2A)	1510(2)	5874(2)	4724(2)	54(1)
O(3A)	1289(2)	5117(2)	2996(2)	57(1)	N(2A)	3154(3)	8888(3)	4716(3)	44(1)
C(9A)	2229(3)	7010(3)	3784(3)	41(1)	C(6A)	2514(4)	10791(4)	5126(4)	56(1)
O(1A)	2469(3)	7941(2)	2534(2)	67(1)	C(8A)	2174(4)	7106(3)	2736(3)	49(1)
C(7A)	2690(3)	7918(3)	4692(3)	41(1)	C(5A)	2365(5)	11750(5)	5146(5)	81(2)
C(10A)	1681(3)	6007(3)	3903(3)	44(1)	C(2A)	4339(4)	11679(4)	6253(5)	83(2)
C(1A)	3497(4)	10729(4)	5673(3)	50(1)	C(13A)	2844(5)	5072(4)	2395(5)	86(2)
C(11A)	1704(4)	5160(4)	2108(4)	60(2)	C(12A)	907(5)	4258(4)	1144(4)	99(2)
C(4A)	3152(6)	12674(6)	5697(6)	110(3)	C(3A)	4130(6)	12665(5)	6229(6)	115(3)

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

Bond	Å	Bond	Å
O(4C)-C(10C)	1.381(5)	N(2B)-C(7B)	1.298(5)
O(4C)-C(11C)	1.469(5)	N(2B)-N(1B)	1.416(4)
O(4B)-C(10B)	1.386(5)	N(1B)-C(1B)	1.417(5)
O(4B)-C(11B)	1.453(5)	N(2C)-C(7C)	1.311(4)
O(2C)-C(8C)	1.221(5)	N(2C)-N(1C)	1.413(4)
O(3C)-C(8C)	1.382(5)	N(1C)-C(1C)	1.420(5)
O(3C)-C(11C)	1.440(5)	N(1A)-N(2A)	1.415(4)
O(2B)-C(10B)	1.229(5)	N(1A)-C(1A)	1.416(6)
O(3B)-C(8B)	1.383(5)	N(2A)-C(7A)	1.302(5)
O(3B)-C(11B)	1.448(6)	O(3A)-C(10A)	1.384(4)
O(1B)-C(8B)	1.236(5)	C(9B)-C(7B)	1.402(5)
O(1C)-C(10C)	1.228(4)	C(9C)-C(7C)	1.395(5)
O(1A)-C(8A)	1.224(5)	C(9A)-C(7A)	1.398(5)
O(4A)-C(11A)	1.454(6)	–	–
Angles	**(º)**	**Angles**	**(º)**
N(2B)-C(7B)-C(9B)	125.8(4)	C(7A)-N(2A)-N(1A)	121.8(4)
N(2C)-C(7C)-C(9C)	125.7(4)	C(7C)-N(2C)-N(1C)	121.5(3)
N(2A)-C(7A)-C(9A)	126.1(4)	C(7B)-N(2B)-N(1B)	120.7(4)
N(2A)-N(1A)-C(1A)	115.2(4)	N(2C)-N(1C)-C(1C)	115.6(3)
N(2B)-N(1B)-C(1B)	114.5(3)	–	–

ing diagram, with a centroid-centroid separation of 4.947, 4.933 and 4.958 Å, respectively (Table-5). In solid state, all above extensive hydrogen bond stabilize the crystal structure twelve intermolecular hydrogen bonds (Table-4).

ACKNOWLEDGEMENTS

The authors thank the Development Plan of Science and Technology of Weifang for support (201003039).

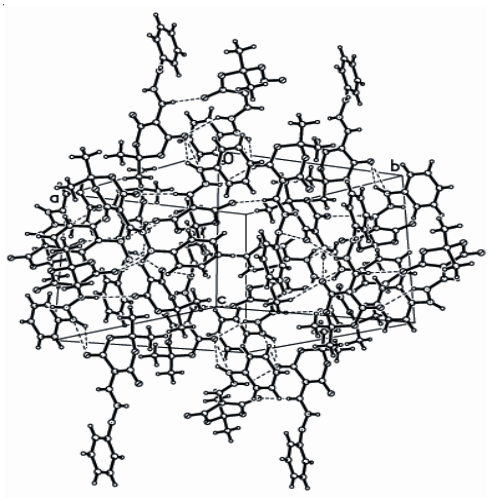


Fig. 1. Molecular structure with atomic numbering scheme

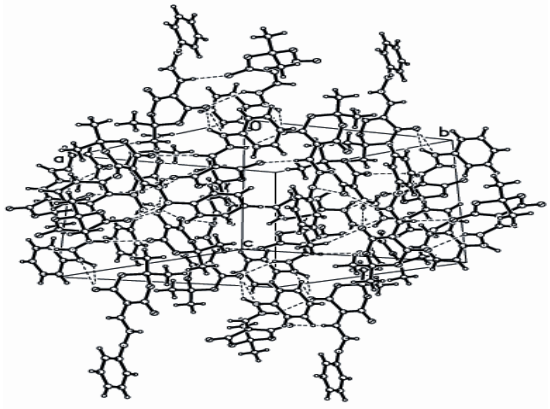


Fig. 2. View of crystal packing

TABLE-4
INTERMOLECULAR INTERACTION DISTANCES (Å)

D-H-A	Symmetry	D-H	H···A	D···A	D-H···A
C(13A) -- H(13I)···O(2B)	1-x, 1-y, -z	0.9585	2.5924	3.502(6)	158.53
C(13B) -- H(13E)···O(1C)	1-x, 1-y, -z	0.9595	2.5738	3.486(7)	158.94
C(13C) -- H(13C)···O(1A)	1-x, 1-y, -z	0.9592	2.6000	3.512(6)	158.97
C(7A) -- H(11#)···O(1C)	1-x, 1-y, 1-z	0.9302	2.5282	3.457(5)	176.40
C(7B) -- H(7A)···O(1A)	x, -1+y, z	0.9295	2.5163	3.444(5)	175.92
C(7C) -- H(3#)···O(2B)	1+x, y, z	0.9301	2.5019	3.431(5)	176.71
N(2A) -- H(10#)···O(1B)	x, 1+y, z	0.8597	2.3657	3.070(5)	139.44
N(1A) -- H(9#)···O(1B)	1-x, 1-y, 1-z	0.8598	2.3739	2.929(5)	122.64
N(2B) -- H(2A)···O(2C)	-1+x, y, z	0.8589	2.3611	3.062(5)	139.00
N(1C) -- H(2#)···O(2A)	1+x, y, z	0.8596	2.380	2.934(5)	122.58
N(1B) -- H(1A)···O(2C)	1-x, -y, -z	0.8599	2.4037	2.946(5)	121.53
N(2C) -- H(1#)···O(2A)	1-x, 1-y, 1-z	0.8597	2.3603	3.059(5)	138.61
C(7A) -- H(11#)···O(2A)	intra	0.9302	2.5319	2.861(5)	101.12
C(7B) -- H(7A)···O(1B)	intra	0.9295	2.5452	2.867(5)	100.71
C(7C) -- H(3#)···O(2C)	intra	0.9301	2.5403	2.862(5)	100.62
N(2A) -- H(10#)···O(1A)	intra	0.8597	2.1257	2.752(5)	129.32
N(2B) -- H(2A)···O(2B	intra	0.8589	2.1122	2.734(5)	128.81
N(2C) -- H(1#)···O(1C)	intra	0.8597	2.1008	2.726(5)	129.13

TABLE-5
π···π STACKING INTERACTIONS

Ring	Symmetry	Centroid-to centroid distance (Å)	Perpendicular distance of Cg(I) on ring J (Å)	Perpendicular distance of Cg (J) on ring I(Å)	Dihedral Angle (β) between Planes I and J (º)
Cg(4)···Cg(5)	-x,1-y,1-z	4.947	4.730	3.043	17.03
Cg(6)···Cg(4)	1+x,-1+y,z	4.933	4.707	3.017	17.42
Cg(5)···Cg(6)	-x,1-y,1-z	4.958	4.738	3.047	17.13

Cg(4): C(1A) > C(2A) > C(3A) > C(4A) > C(5A) > C(6A); Cg(5): C(1B) > C(2B) > C(3B) > C(4B) > C(5B) > C(6B); Cg(6) C(1C) > C(2C) > C(3C) > C(4C) > C(5C) > C(6C)

REFERENCES

1. M. Zhou, R. Li and Z.Y. Ding, *Acta Crystallogr. E*, **65**, o2171 (2009).
2. A.S. Ivanov, *Chem. Soc. Rev*., **37**, 789 (2008).
3. L.E. da Silva, A.C. Joussef, L.L. Silva, S. Foro and B. Schmidt, *Acta Crystallogr. E*, **62**, o3866 (2006).
4. T. Watanabe, T.F. Knöpfel and E.M. Carreira, *Org. Lett*., **5**, 4557 (2003).
5. W.L. Zeng, *Asian J. Chem*., **25**, 8566 (2013).
6. W.L. Zeng, *Acta Crystallogr. E*, **67**, o1937 (2011).
7. W.L. Zeng, *Acta Crystallogr. E*, **67**, o1351 (2011).
8. W.L. Zeng, *Acta Crystallogr. E*, **66**, o2319 (2010).
9. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
10. Siemens, Area Detector Control and Integration Software, USA (1996).