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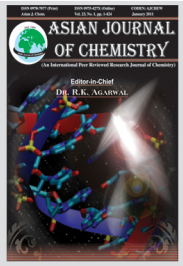

Synthesis and Crystal Structure of 3-(3,4-Dimethylbenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione

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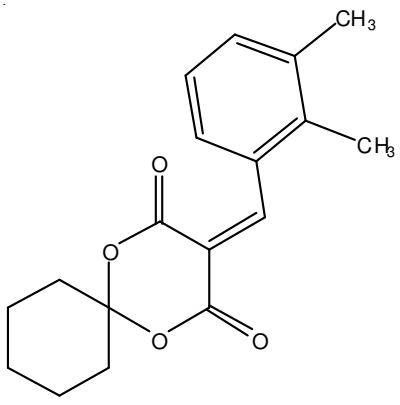
A new spiro compound 3-(3,4-dimethylbenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione was prepared by 1,5-dioxaspiro[5.5]undecane-2,4-dione with 3,4-dimethylbenzaldehyde in ethanol and its crystal structure was determined by X-ray crystallographic techniques. It crystallizes in monoclinic, space group Cc with a = 27.437(6) Å, b = 11.471(2) Å, c = 21.196(4) Å, β = 109.85(3)°, $C_{18}H_{20}O_4$, Mr = 300.34, V = 6275(2) Å^3, Z = 16, Dc = 1.271 g/cm^3, F(000) = 2556, μ = 0.089 mm^{-1}. The 1,3-dioxane ring is in a distorted envelope conformation while cyclohexane ring assumes a highly symmetric chair conformation.

Key Words: Synthesis, Crystal structure, 1,5-Dioxaspiro[5.5]undecane-2,4-dione, Spiro compounds.

INTRODUCTION

Spiro compounds have attracted the attention of scholars and scientists owing to their potential applications in medicine[1-4], catalysis and optical material[5,6]. Recently, the design and synthesis of spiro compounds were stimulated by an increasing interest due to their pronounced biological activities such as pheromones, antibiotics, antineoplastics[7], herbicides with low toxicity to microorganisms[8], *etc*. However, to the best of our knowledge, the spiro compounds containing the 1,5-dioxaspiro[5.5]undecane-2,4-dione and 3,4-dimethylphenyl fragments in one molecule have never reported. In this paper, we report the synthesis and crystal structure of the 3-(3,4-dimethylbenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione (**I**).



(**I**)

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. Melting points were measured by using a melting point apparatus made in Shanghai Instrument Limited Company.

A mixture of 3,4-dimethyl benzaldehyde (1.34 g, 0.01 mol) and 1,5-dioxaspiro[5.5]undecane-2,4-dione (1.84 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 41 % m.p. 118.6-118.9 ºC. Anal. calcd. (%) for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found (%): C, 71.68; H, 6.68. The single crystal suitable for X-ray diffraction analysis was obtained by evaporation for petroleum ether and ethyl acetate (2:1 = v/v) after a few days.

Data collection and structure determination: A selected crystal of the present compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 293 K, using a graphite monochromator MoK_α (λ = 0.071073 nm) radiation with an ω scan mode. A total of 27656 reflections were collected and 13309 were independent (R_{int} = 0.0662) in the range of $3.01 < \theta < 27.48°$, of which 3755 reflections were observed with $I > 2\sigma(I)$.

The structure of the 3-(3,4-dimethylbenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione 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.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE 3-(3,4-DIMETHYLBENZYLIDENE)-1,5-DIOXASPIRO[5.5]UNDECANE-2,4-DIONE

Empirical formula	$C_{18}H_{20}O_4$
Formula weight	300.34
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 27.437(6) Å α = 90°, b = 11.471(2) Å β = 109.85(3)°, c = 21.196(4) Å γ = 90°
Volume (Å^3) Z	6275(2) ,16
Calculated density (g/cm^3)	1.271
Absorption coefficient (mm^{-1})	0.089
F(000)	2560
Crystal size (mm)	0.22 × 0.18 × 0.12 mm
Theta range for data collection (°)	3.01-27.48
Limiting indices	-35 ⇐ h ⇐ 35, -14 ⇐ k ⇐ 14, -27 ⇐ l ⇐ 27
Reflections collected/unique	27656 / 13309 [$R_{(int)}$ = 0.0662]
Completeness to theta = 28.24	99.3 %
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	13309/2/793
Goodness-of-fit on F^2	0.973
Final R indices [I > 2σ(I)] R indices (all data)	R1 = 0.0943, wR^2 = 0.2488 R1 = 0.2306, wR^2 = 0.3500
Largest diff. peak and hole (Einstein Å^{-3})	0.691 and-0.444

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the present 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.

There are four symmetry-independent molecules, A, B, C and D in the asymmetric unit of (**I**) and these are depicted in Fig. 1. The corresponding bond lengths and angles for the independent molecules agree well with each other. The C9=C10 distances of 1.348(12), 1.330(12), 1.355(12) and 1.360(12) Å in molecules A, B, C and D, respectively, confirm the localization of the double bond at this position. The C6-C9 distances of 1.466(13), 1.481(13), 1.439(13) and 1.427(13) Å in molecules A, B, C and D, respectively, are in good agree with the values reported in the literature[11]. Each molecule consists of 1,3-dioxane ring and cyclohexane ring and they do not share a common plane. The core skeletons of the four molecules have the same almost identical conformations, with minor differences in the puckering of some rings. The six-membered rings have chair conformations, with puckering

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

Bond	Å	Bond	Å
C(10B)-C(9B)	1.330(12)	C(9C)-C(10C)	1.355(12)
C(6B)-C(9B)	1.481(13)	C(9C)-C(6C)	1.439(13)
C(9D)-C(10D)	1.360(12)	C(10A)-C(9A)	1.348(12)
C(9D)-C(6D)	1.427(13)	C(6A)-C(9A)	1.466(13)
Angles	(°)	Angles	(°)
C(10A)-C(9A)-C(6A)	129.4(10)	C(10B)-C(9B)-C(6B)	129.0(10)
C(10C)-C(9C)-C(6C)	130.8(9)	C(10D)-C(9D)-C(6D)	130.5(9)

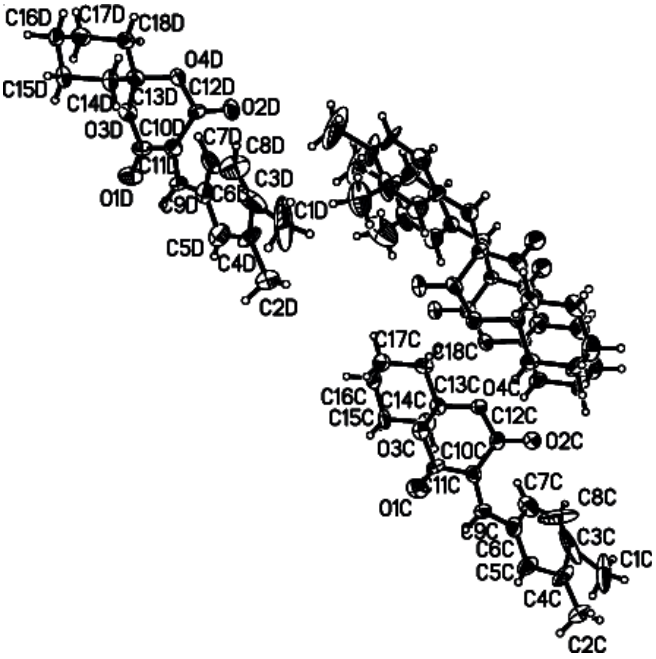


Fig. 1. Molecular structure with atomic numbering scheme

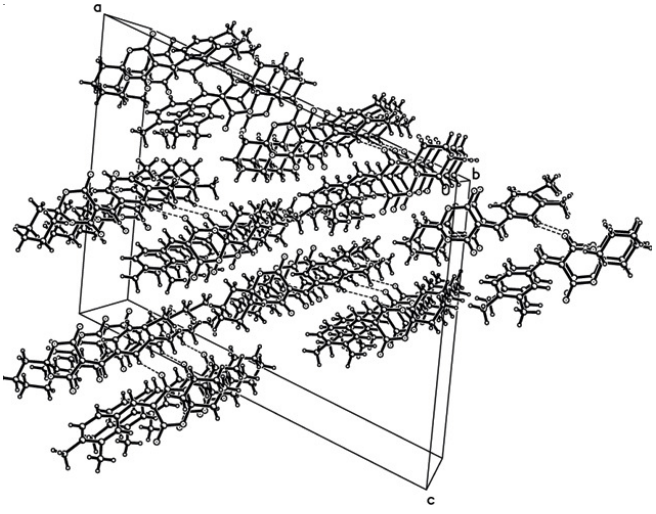


Fig. 2. View of crystal packing

parameters for molecule A [molecule B, C and D in brackets] of Q = 0.541 Å [0.530 Å, 0.485 Å, 0.497 Å], q^2 = 0.533 Å [0.521 Å, 0.471 Å, 0.484 Å], q^3 = -0.09 Å [-0.094 Å, 0.118 Å, -0.110 Å], ϑ = 99.6° [100.2°, 75.9°, 102.8°], φ = 120.53° [120.31°, 301.84°, 124.02°] for the atom sequence 13A-18A [13B-18B, 13C-18C, 13D-18D]. There are no classic hydrogen bonds in the crystal lattice.

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

Atom	x	y	Z	U (eq)	Atom	x	y	Z	U (eq)
O(4B)	1308(2)	5743(5)	93(3)	48(2)	O(3A)	1207(2)	-118(5)	1046(3)	51(2)
O(3B)	1212(2)	4887(5)	1049(3)	53(2)	O(3D)	5156(2)	-1730(5)	6979(3)	55(2)
C(13B)	1049(3)	4844(7)	334(4)	41(2)	O(2D)	4608(3)	-2685(7)	5083(3)	74(2)
C(10B)	2079(3)	5130(7)	998(4)	42(2)	O(2A)	2075(3)	1403(6)	115(4)	75(2)
O(2B)	2076(3)	6409(6)	116(4)	78(2)	C(12D)	4743(4)	-2580(8)	5674(5)	51(2)
C(18B)	893(4)	3599(10)	-664(5)	69(3)	C(13A)	1047(3)	-157(8)	326(4)	45(2)
C(12B)	1832(4)	5826(8)	374(5)	56(3)	C(10A)	2071(3)	124(7)	993(4)	42(2)
C(14B)	1135(3)	3668(7)	78(4)	51(2)	C(13D)	5433(4)	-2622(8)	6751(5)	51(2)
C(15B)	486(3)	5205(9)	86(5)	59(3)	O(1A)	1864(3)	-176(7)	1995(3)	81(2)
C(6B)	2889(4)	4057(10)	1704(5)	60(3)	C(9D)	3914(3)	-2696(8)	5908(4)	51(2)
C(11B)	1730(4)	4898(8)	1406(5)	54(2)	C(15A)	492(3)	201(9)	99(5)	61(3)
O(1B)	1866(3)	4835(7)	1999(3)	75(2)	C(6A)	2881(4)	-955(10)	1708(5)	59(3)
C(16B)	231(4)	5051(11)	-677(5)	78(3)	C(12A)	1823(4)	830(8)	378(5)	60(3)
C(17B)	335(5)	3873(9)	-929(5)	74(3)	C(18A)	894(4)	-1399(9)	-659(5)	69(3)
C(9B)	2578(4)	4858(8)	1171(5)	62(3)	C(14A)	1136(4)	-1333(8)	82(4)	52(2)
C(3B)	3515(8)	2609(18)	2702(6)	130(10)	C(10D)	4416(4)	-2354(8)	6071(5)	57(3)
C(7B)	3396(4)	4179(12)	2000(6)	87(4)	C(14D)	5341(4)	-3821(7)	6996(4)	56(2)
C(5B)	2701(5)	3185(12)	1962(6)	90(4)	C(17D)	6235(4)	-2410(10)	7767(5)	69(3)
C(1B)	3897(9)	1970(20)	3290(8)	273(19)	C(17A)	333(5)	-1102(11)	-925(5)	85(4)
C(8B)	3720(6)	3589(16)	2471(7)	135(8)	C(9A)	2577(4)	-159(9)	1179(5)	61(3)
C(4B)	3004(7)	2438(12)	2447(6)	112(6)	C(11A)	1721(4)	-100(7)	1395(4)	50(2)
O(4C)	262(2)	2608(5)	1030(3)	54(2)	C(18D)	6000(4)	-2318(9)	7003(5)	57(3)
O(3C)	156(2)	1730(5)	1980(3)	54(2)	C(15D)	5572(4)	-3942(9)	7771(4)	62(3)
O(2C)	-390(3)	2662(7)	91(3)	71(2)	O(1D)	4412(3)	-1069(6)	6967(4)	82(2)
C(12C)	-250(4)	2596(8)	697(5)	54(2)	C(11D)	4635(3)	-1702(8)	6697(5)	51(2)
C(9C)	-1088(3)	2679(8)	902(4)	50(2)	C(6D)	3602(4)	-3413(10)	5373(5)	66(3)
C(11C)	-363(3)	1694(8)	1705(5)	52(2)	C(16D)	6147(4)	-3621(10)	7985(5)	72(3)
C(6C)	-1397(4)	3424(10)	372(5)	68(3)	C(16A)	237(4)	69(12)	-660(6)	84(4)
O(1C)	-591(3)	1070(6)	1968(4)	83(2)	C(7D)	3823(5)	-4393(11)	5169(5)	75(3)
C(13C)	443(4)	2617(8)	1754(4)	49(2)	C(5A)	2700(5)	-1847(11)	1978(6)	95(4)
C(16C)	1142(4)	3631(10)	2994(5)	75(3)	C(5D)	3049(4)	-3173(11)	5119(6)	88(4)
C(14C)	337(4)	3819(6)	1998(4)	51(2)	C(7A)	3393(5)	-834(11)	2006(5)	76(3)
C(10C)	-585(4)	2350(8)	1075(5)	56(3)	C(4D)	2787(4)	-4229(11)	4500(6)	89(4)
C(5C)	-1949(4)	3177(11)	117(5)	88(4)	C(3A)	3559(8)	-2339(18)	2712(6)	161(11)
C(17C)	1238(4)	2428(10)	2765(5)	70(3)	C(3D)	3138(6)	-5040(11)	4400(7)	120(6)
C(7C)	-1158(5)	4410(11)	170(6)	81(4)	C(2D)	2238(3)	-3914(9)	4203(5)	81(3)
C(18C)	1003(4)	2317(10)	2005(5)	59(3)	C(8D)	3590(5)	-5288(13)	4685(9)	132(6)
C(15C)	572(4)	3942(9)	2774(4)	62(3)	C(2C\)	-2762(4)	3929(8)	-795(5)	80(3)
C(4C)	-2205(4)	4194(13)	-478(6)	105(5)	C(1D)	2661(8)	-5809(17)	3800(6)	232(13)
C(3C)	-1864(12)	5037(10)	-589(9)	153(9)	C(1C)	-2332(8)	5822(16)	-1189(6)	201(12)
C(8C)	-1421(5)	5280(20)	-346(13)	203(14)	C(2B)	2871(8)	1581(13)	2802(10)	193(9)
O(4A)	1307(2)	743(5)	99(3)	50(2)	C(2A)	2886(7)	-3363(12)	2807(7)	126(5)
O(4D)	5255(3)	-2610(5)	6025(3)	56(2)	C(8A)	3720(6)	-1401(16)	2475(6)	131(8)
C(1A)	3889(9)	-3057(19)	3282(8)	306(18)	C(4A)	3025(8)	-2555(12)	2453(6)	118(6)

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