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

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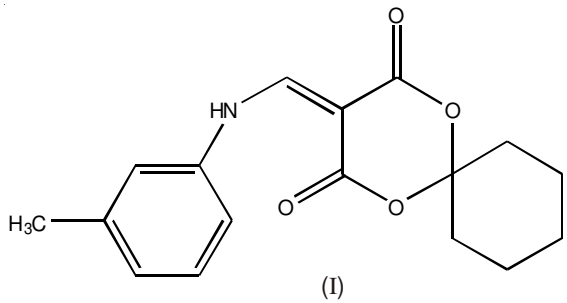
A new N,O-containing spiro compound 3-((*m*-tolylamino)methylene)-1,5-dioxaspiro[5.5]undecane-2,4-dione was synthesized and its crystal structure was determined by X-ray crystallographic techniques. The compound crystallizes in triclinic, space group P-1 with a = 7.0264 (14) Å, b = 7.8523 (16) Å, c = 14.102 (3) Å, α = 94.75 (3)°, β = 98.14 (3)°, γ = 96.29 (3)°, $C_{17}H_{19}NO_4$, Mr = 301.33, V = 761.7 (3) Å^3, Z = 2, Dc = 1.314 g/cm^3, F (000) = 320, μ(MoKα) = 0.094 mm^{-1}, the final R = 0.0496 and wR = 0.3294. The 1,3-dioxane ring is in a distorted envelope conformation while cyclohexane ring assumes a highly symmetric chair conformation. There exist some intra- and intermolecular hydrogen bonds, C-H···π supramolecular interactions and π···π stacking interactions in the title compound. All above hydrogen bonds and intermolecular interactions play a significant role in stabilizing the crystal structures.

Keywords: 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 antimicrobial, anxiolytic, antineoplastic, analgesic activity, *etc*.[7-9]. For these reasons, our group have developed a new simple strategy towards the construction of various oxaspirocyclic compounds[10-12]. However, to the best of our knowledge, among so many reported spiro-compounds, O, N- containing spiro compounds derived from 1,5-dioxaspiro [5.5]undecane-2,4-dione are rare. In this paper, we report the synthesis and crystal structure of the title compoud, 3-((*m*-tolylamino)methylene)-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. 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 1,5-dioxaspiro[5.5]undecane-2,4-dione (1.84 g, 0.01 mol)) was stirred in ethanol (30 mL) for 2 h at reflux temperature. Then the *m*-toluidine (1.07 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 38 %. m.p.: 125.2-126.6 °C. The colorless and block single crystal was obtained by evaporation for petroleum ether and ethyl acetate (1:1 = 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 7471 reflections were collected and 3456 were independent (R_{int} = 0.0496) in the range of 3.09 < θ < 27.48°, of which 1302 reflections were observed with I > 2σ(I).

The structure of the compound **I** was solved by direct methods and refined by full-matrix least-squares on F^2 using

the SHELXTL software package[13]. 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[14]. The crystal and experimental data are shown in Table-1.

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

Empirical formula	$C_{17}H_{19}NO_4$
Formula weight	301.33
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.0264(14) Å; α = 94.75 (3)° b = 7.8523(16) Å; β = 98.14 (3)° c = 14.102(3) Å; γ = 96.29 (3)°
Volume (Å^3), Z	761.7(3), 2
Calculated density (g/cm^3)	1.314
Absorption coefficient (mm^{-1})	0.094
F (000)	320
Crystal size (mm)	0.26 × 0. 18 × 0.16 mm
Theta range for data collection (°)	3.09-27.48
Limiting indices	-8 < = h < = 9; -10 < = k < = 9; -18 < = l < = 18
Reflections collected/unique	7471/3456 [R(int) = 0.0496]
Completeness to theta = 27.48	99.1 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3456/0/199
Goodness-of-fit on F^2	1.689
Final R indices [I > 2σ(I)]	R_1 = 0.1267, wR_2 = 0.3292
R indices (all data)	R_1 = 0.2245, wR_2 = 0.3854
Largest diff. peak and hole (Einstein Å^{-3})	0.684 and-0.300

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.

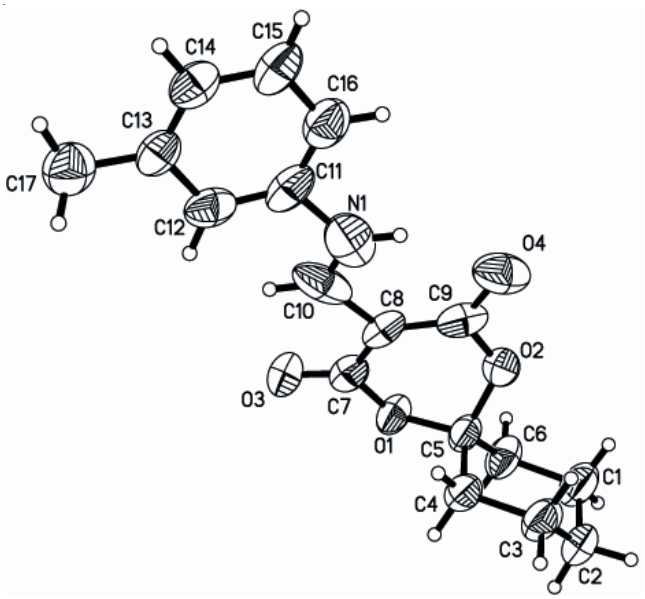


Fig. 1. Molecular structure with atomic numbering scheme

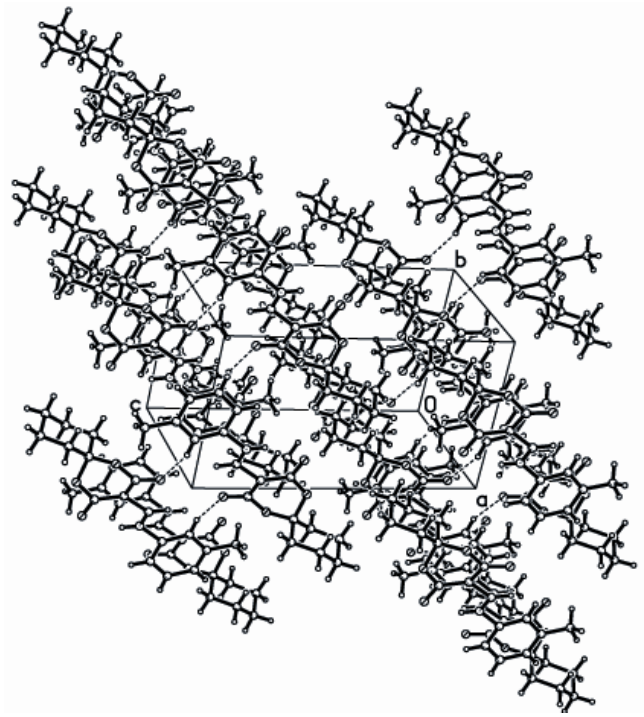


Fig. 2. View of crystal packing

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(2)	1649(5)	549(5)	6416(3)	89(1)	C(7)	430(8)	-304(8)	8128(5)	88(2)
O(1)	254(5)	-1470(4)	7336(3)	86(1)	C(4)	3542(8)	-1606(7)	7047(4)	89(2)
C(8)	1374(8)	1319(8)	8046(5)	90(2)	C(2)	4053(11)	-2702(9)	5413(5)	119(2)
C(6)	714(9)	-2357(7)	5765(4)	99(2)	C(16)	2987(9)	6807(11)	9747(5)	111(2)
C(5)	1558(7)	-1224(6)	6651(4)	79(2)	C(14)	3202(7)	7577(8)	11412(5)	94(2)
N(1)	2284(8)	3896(11)	8978(5)	137(2)	C(10)	1581(8)	2521(10)	9034(7)	136(3)
C(12)	2484(7)	4630(8)	10810(6)	100(2)	C(15)	3286(9)	8044(10)	10515(5)	112(2)
C(11)	2558(8)	5162(11)	9917(6)	100(2)	C(3)	4892(8)	-1504(8)	6308(5)	103(2)
O(3)	-317(7)	-753(6)	8802(3)	128(2)	C(1)	2051(10)	-2313(10)	5007(5)	118(2)
C(13)	2794(7)	5927(8)	11598(4)	89(2)	C(17)	2673(10)	5456(9)	12562(6)	127(2)
O(4)	2425(6)	3269(5)	6971(4)	132(2)	C(7)	430(8)	-304(8)	8128(5)	88(2)
C(9)	1872(8)	1834(8)	7171(6)	100(2)	–	–	–	–	–

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(3)···Cg(3)	-x,1-y,2-z	4.450	3.522	3.522	37.68
Cg(3)···Cg(3)	1-x,1-y,2-z	4.385	3.413	3.413	38.90
Cg(3): C(1)>C(2)> C(3)>C(4)> C(5)>C(6)					

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

Bond	Å	Bond	Å
O(2)-C(9)	1.384(7)	N(1)-C(10)	1.151(8)
O(2)-C(5)	1.454(6)	N(1)-C(11)	1.564(9)
O(1)-C(7)	1.367(6)	O(3)-C(7)	1.208(6)
O(1)-C(5)	1.433(5)	O(4)-C(9)	1.219(7)
C(8)-C(9)	1.408(9)	C(8)-C(10)	1.596(10)
Angles	(º)	Angles	(º)
C(10)-N(1)-C(11)	115.9(8)	C(7)-C(8)-C(10)	110.6(6)
N(1)-C(10)-C(8)	112.4(8)	C(9)-C(8)-C(10)	126.1(6)

As can be seen from the crystal structure (Fig. 1), the central C(10) atom is linked by 1,5-dioxaspiro[5.5]undecane-2,4-dione group and ***m*-tolylamino** ring, forming the N(1)-C(10)-C(8) bond angle of 122.4 (8(5)º. The 1,3-dioxane rings of the title compound are both in a distorted screw-boat conformation. While the cyclohexane rings of the two compounds both exhibit a chair-like configuration, with puckering parameters[15] for Q = 0.553 (7) Å, q^2 = 0.024 (7) Å), q^3 = 0.552 (7) Å, J = 0.552 (7), J = 108 (16)º.

As shown in Table-4, there exists one type of N-H···O intra- and one type of C-H···O intermolecular hydrogen bond in the title compound. The salient feature in the crystal packing of the title compound is that there is still two types of C-H···π supramolecular interactions and two types of π···π stacking interactions (Table-5). In the crystal lattices, all above hydrogen bonds and intermolecular interactions play a significant role in stabilizing the crystal structures.

TABLE-4
INTERMOLECULAR INTERACTION DISTANCES (Å)

D-H-A	Symmetry	D-H	H···A	D···A	D-H···A
N(1)-H(1A)···O(4)	intra	0.8596	2.1368	2.850(9)	140.08
C(12)-H(12A)···O(3))	-x,-y,2-z	0.9300	2.4975	3.374(8)	157.10
N(1)-H(1A)···phenyl ring	1-x,1-y,2-z	0.8600	3.305	3.391	88.31
C(10)-H(10A)··· phenyl ring	-x,1-y,2-z	0.9300	3.188	3.423	96.70

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