

Synthesis, Crystal and Molecular Structure of 2',3',3'-Tribromo-2',3'-dihydrospiro[1,3-dioxolane-2,1'-indene]

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Abstract The crystal structure of 2',3',3'-tribromo-2',3'-dihydrospiro[1,3-dioxolane-2,1'-indene], ($C_{11}H_9Br_3O_2$), has been determined by means of single-crystal X-ray diffraction methods. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters: $a = 8.9799(4)$, $b = 11.3368(8)$, $c = 12.4233(9)$ Å, $\beta = 94.938(4)^\circ$, $V = 1260.04(14)$ Å³, $Z = 4$. The cyclopentane ring fused to the benzene ring adopts an envelope conformation with C11 at the tip of the envelope. The crystal structure is stabilized by C–H⋯Br and C–H⋯O interactions. The C atoms of the CH₂ groups of the 1,3-dioxolane ring, are disordered over two sites with an occupancy ratio of 0.62(7):0.38(7). A semiempirical quantum-mechanical calculation was carried out using the CNDO approximation.

Keywords Single-crystal X-ray diffraction · Crystal structure · Hydrogen bonding · CNDO

Introduction

Indanes are important class of molecules due to the pharmacological and medicinal properties [1–4] as well as natural product chemistry [5]. Brominations of hydrocarbons are important processes in synthetic chemistry [6–10]. The materials obtained from bromination of hydrocarbons have numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals [11]. Bromoindanes are important key intermediates in the industrial and laboratory preparation of hydroxy and

epoxide compounds [12], and of indenone and fluorenone compounds [13].

In continuation of our investigations of the synthesis and structure of the bromoindanes, we describe herein the synthesis and structure of a new compound 2',3',3'-tribromo-2',3'-dihydrospiro[1,3-dioxolane-2,1'-indene] (Scheme 1). In addition, a semiempirical quantum-mechanical calculation was carried out using the CNDO approximation. The theoretical CNDO and experimental X-ray structural results has been compared with each other.

Experimental

Synthesis

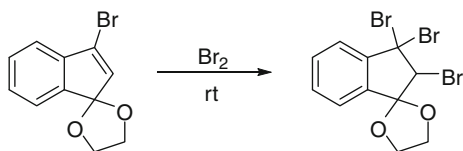
Melting points were determined on a Büchi model 530 apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on 400 (100) MHz spectrometers. Mass spectra (EI) were recorded at 70 eV as *m/z*. All solvents were dried and distilled before use. Column chromatography was performed on silica gel 60 (70–230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminium plates. The substance reported in this paper is in its racemic form.

To a magnetically stirred solution of starting material 3'-bromospiro[1,3-dioxolane-2,1'-indene] (100 mg, 0.4 mmol) in dichloromethane (2 ml) at room temperature was added, dropwise, a solution of bromine (70 mg, 0.44 mmol) in dichloromethane (0.5 ml) over the course of 1 min. After stirring for 10 min at room temperature, the solvent was evaporated and the crude product, 160 mg (98 %) of tribromide, was crystallized from ether/hexane (3:1). m.p. 380–382 K.

¹H NMR (400 MHz, CDCl₃): 7.78 (d, $J = 7.7$ Hz, Hz), 7.55 (td, $J = 1.0$ Hz, $J = 7.7$ Hz, 2H), 7.42 (td, $J = 1.0$ Hz, $J = 7.7$ Hz, 2H), 7.32 (d, $J = 7.7$ Hz, 2H), 5.06

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Scheme 1 Synthesis of 2',3',3'-tribromo-2',3'-dihydrospiro[1,3-dioxolane-2,1'-indene]

(s, 2H), 4.47 (m, 2H), 4.37 (m, 2H), 4.29 (m, 2H), 4.22 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): 145.0, 136.2, 131.6, 131.1, 125.8, 122.9, 110.9, 70.5, 66.83, 66.78, 59.6. IR (KBr, cm^{-1}): 2956, 2895, 1465, 1316, 1273, 1193, 1149, 1090, 1052, 1027, 966, 948.

X-Ray Structural Analysis

Crystallographic data are given in Table 1. Pale yellow block crystal (0.2, 0.2, 0.2 mm) was used for data collection. Diffraction data for the title compound were collected at room temperature ($T = 294(2)$ K) using a Rigaku R-AXIS RAPID-S diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization and absorption effects using CrystalClear [14]. The structure was solved by the direct method using SIR97 [15] and was refined by full matrix least squares based on F^2 using SHELXL-97 [16]. The molecular graphic were drawn using the ORTEP-3 for Windows [17] and PLATON programs [18].

H-atoms were positioned geometrically and refined using a riding model with $\text{C-H} = 0.93$ and 0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. All non-hydrogen atoms were refined anisotropically. Two poorly fitted reflections (4 9 0) and (7 2 0) were omitted from the refinement. The atoms, C1 and C2, of the $-\text{C}-\text{C}-$ bond between the oxygen atoms in the 1,3-dioxolane ring, are disordered over two sites with site-occupancy factors of 0.62(7) and 0.38(7). In the final difference Fourier map, the highest peak is 0.86 Å from atom Br_3 and the deepest hole is 1.05 Å from atom Br_2 .

Results and Discussion

Crystal Structure

As shown in the title compound, (Fig. 1), the cyclopentane ring (C4–C9) fused to the benzene ring of the nine-membered ring system (C3–C11) adopts an envelope conformation with C11 at the tip of the envelope [the puckering parameters [19] are $Q(2) = 0.330(11)$ Å and $\phi(2) = 141.5(19)^\circ$].

The C atoms of the CH_2 groups of the 1,3-dioxolane ring, are disordered over two sites with an occupancy ratio of 0.62(7):0.38(7). In the disordered 1,3-dioxolane ring, its minor component adopts an envelope conformation with

Table 1 Crystal data and experimental details

Empirical formula	$\text{C}_{11}\text{H}_9\text{Br}_3\text{O}_2$
Formula weight	412.88
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.9799(4)$ Å, $\alpha = 90^\circ$ $b = 11.3368(8)$ Å, $\beta = 94.938(4)^\circ$ $c = 12.4233(9)$ Å, $\gamma = 90^\circ$
Volume	$1260.04(14)$ Å ³
Z	4
Density (calculated)	2.177 Mg m^{-3}
Absorption coefficient	9.59 mm^{-1}
F (000)	784
Crystal shape and color	Block, pale yellow
Crystal size	$0.20 \times 0.20 \times 0.20$ mm ³
θ range for data collection	$2.4\text{--}26.5^\circ$
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	26249
Independent reflections	2606 [$R_{\text{int}} = 0.176$]
Completeness to $\theta = 26.5^\circ$	99.8%
Absorption correction	Multi-scan
Max. and min. transmission	0.250 and 0.250
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2606/11/165
Calculated weights, w	$1/[\sigma^2(F_o^2) + (0.0708P)^2 + 2.167P]$, where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.07
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.069$, $wR_2 = 0.193$
Extinction coefficient	0.004602
Largest diff. peak and hole	0.60 and -0.91 e.Å ⁻³

C3 at the tip of the envelope [the puckering parameters are $Q(2) = 0.20(3)$ Å and $\phi(2) = 31(9)^\circ$].

In the title compound, the values of the C–Br bond lengths range from $1.915(10)$ to $1.972(10)$ Å. The relatively wide range of the Br–C–C bond angles are within the range $108.6(7)\text{--}116.2(7)^\circ$ and this may indicate repulsion between the neighbouring Br atoms. In a related structure (1*RS*,2*SR*)-1,2,4,5,7-pentabromo-5-methoxyindane [9], the five Br–C distances vary from $1.884(7)^\circ$ to $1.980(7)^\circ$ Å. The Br–C–C angles are within the range $107.2(5)^\circ\text{--}117.0(4)^\circ$. In trans,trans,trans-2,3,5,8-tetrabromo-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene [20], very similar values for the corresponding parameters [$1.938(5)$ Å and $107.0(3)\text{--}121.6(4)^\circ$, respectively] were observed. All the bond lengths are within normal values (Table 1) [21].

In the crystal structure, the C–H \cdots Br and C–H \cdots O hydrogen bonding interactions (Table 2) help to stabilize

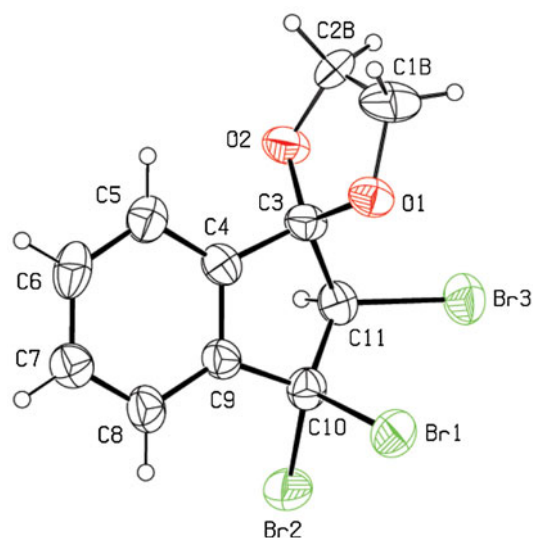


Fig. 1 Molecular structure and atomic numbering scheme for the title compound. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Only the major components of the disordered 1,3-dioxolane ring are shown for clarity

the crystal packing of the title compound. Figure 2 shows the packing and hydrogen bonding in Table 3 of the title compound, along the *a*-axis.

Semiempirical CNDO Calculations

Theoretical calculations were carried out using the semiempirical quantum-mechanical complete neglect of differential overlap (CNDO) method [22]. The spatial view of the single molecule calculated as closed-shell in a vacuum is shown in Fig. 3 with atomic labels. When we compare the theoretical CNDO and experimental X-ray

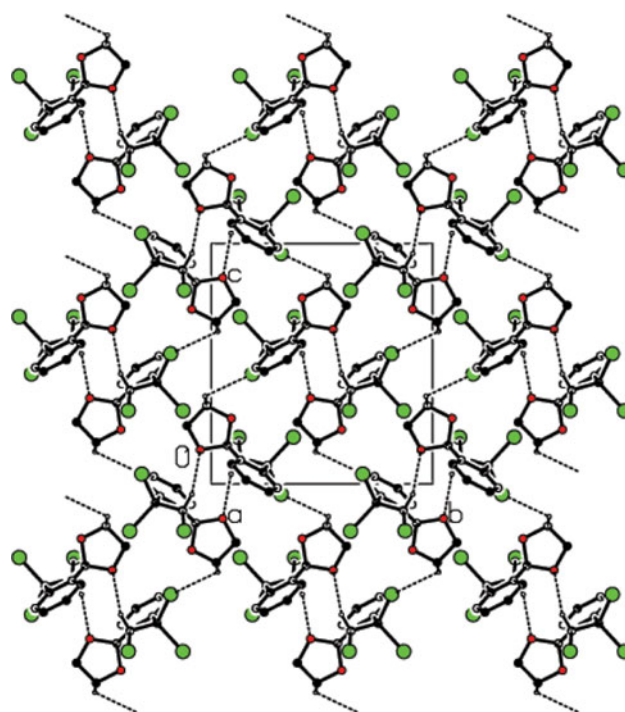


Fig. 2 View of the packing and hydrogen bonding of the title compound, along the *a*-axis. H atoms not involved in hydrogen bonding and the minor components of the disordered 1,3-dioxolane ring are omitted for the sake of clarity

structural results with each other, it is shown that due to the intermolecular interactions in the crystal structure of the title compound, the spatial configurations obtained by the theoretical CNDO and experimental X-rays for the title compound are almost the same (see Figs. 1, 3, Table 2). We may state that the theoretical calculation (based on isolated molecules) of the title compound supports the suggestion

Table 2 Selected geometric parameters (Å, °)

	X-ray	CNDO		X-ray	CNDO
Br1–C10	1.972(10)	2.0108	O1–C1A	1.44(3)	1.4347
Br2–C10	1.955(10)	1.9851	O2–C2B	1.419(19)	–
Br3–C11	1.915(10)	2.0966	O2–C3	1.407(11)	1.4189
O1–C1B	1.424(18)	–	O2–C2A	1.43(3)	1.4320
O1–C3	1.402(11)	1.5548			
C1B–O1–C3	108.8(8)	–	O1–C3–C4	112.6(8)	132.97
C1A–O1–C3	106.6(10)	113.96	O2–C3–C4	112.8(8)	83.03
C2B–O2–C3	108.8(8)	–	O2–C3–C11	109.4(8)	150.26
C2A–O2–C3	106.5(10)	105.28	Br1–C10–C9	108.6(7)	153.18
O1–C1A–C2A	106.3(19)	95.95	Br1–C10–Br2	106.9(5)	62.48
O1–C1B–C2B	107.0(13)	–	Br2–C10–C11	110.9(7)	154.92
O2–C2A–C1A	108(2)	86.89	Br1–C10–C11	114.4(7)	92.53
O2–C2B–C1B	107.2(12)	–	Br2–C10–C9	113.4(7)	92.36
O1–C3–C11	113.7(8)	87.46	Br3–C11–C3	115.1(7)	147.36
O1–C3–O2	108.1(7)	69.02	Br3–C11–C10	116.2(7)	116.74

Table 3 Hydrogen-bond parameters (Å, °)

	D–H	H···A	D···A	D–H···A
C1B–H1B2···Br2 ⁱ	0.97	2.89	3.45(3)	117
C11–H11···O2 ⁱⁱ	0.98	2.55	3.363(12)	140

Symmetry codes: (i) $1/2 + x, 1/2 - y, 1/2 + z$; (ii) $1 - x, -y, -z$

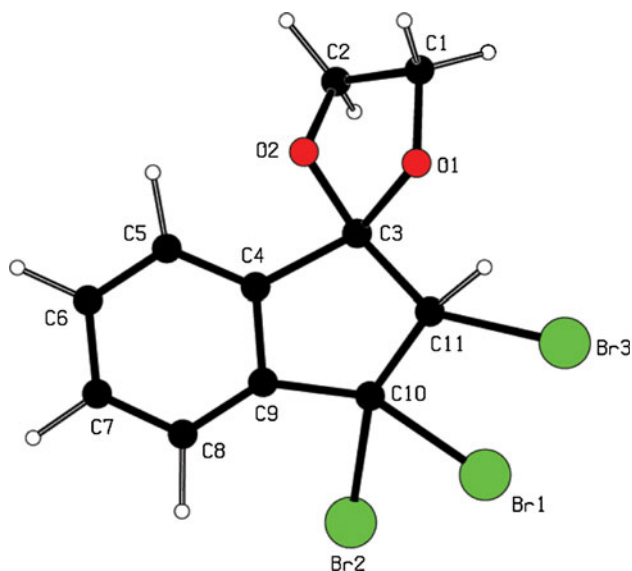


Fig. 3 The spatial view of the title molecule (I), calculated by the CNDO approximation

that the present intra and intermolecular interactions in the title compound influence crystal packing. The HOMO and LUMO energy levels of the title compound are -4.1128 and 0.8545 eV, respectively. Its calculated molecule dipole moment is 8.507 Debye ($1\text{D} = 3.33564 \times 10^{-30}$ C.m.). The charges at atoms C10, C11, O1, O2, Br1, Br2 and Br3 are -0.3025 , -0.3029 , 0.0535 , 0.1285 , 0.2418 , 0.1724 and -0.5880 e⁻, respectively.

Supplementary Material

CCDC 917443 contain the supplementary crystallographic data for this paper. These data can be obtained free of

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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