

## Structure and Conformational Analysis of 5,5-Bis(bromomethyl)-2-phenyl-1,3-dioxane

Sh. Yu. Khazhiev<sup>a</sup>, M. A. Khusainov<sup>a</sup>, R. A. Khalikov<sup>b</sup>, T. V. Tyumkina<sup>c</sup>,  
E. S. Meshcheryakova<sup>c</sup>, L. M. Khalilov<sup>c</sup>, and V. V. Kuznetsov<sup>a,d,\*</sup>

<sup>a</sup> Ufa State Petroleum Technological University, Ufa, Russia

<sup>b</sup> Bashkirian State Medical University, Ufa, Russia

<sup>c</sup> Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia

<sup>d</sup> Ufa State Aviation Technical University, ul. K. Marksa 12, Ufa, 450008 Russia

\*e-mail: kuzmaggy@mail.ru

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**Abstract**—The structure of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane was investigated by the methods of <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy and X-ray analysis. The molecule exists in the chair conformation with the equatorial phenyl group. The routes of interconversion of the ring, free conformational energy and optimal conformation of the phenyl group were determined using computer modeling by the method of DFT (PBE/3ζ). The results are consistent with the data of X-ray analysis.

**Keywords:** 1,3-dioxane, NMR, X-ray analysis, conformational analysis, computer modeling

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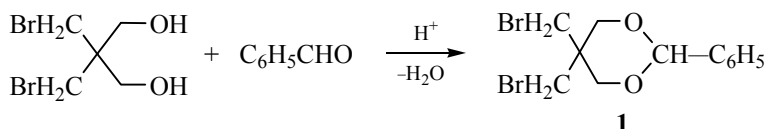
Structural studies of 1,3-dioxanes as classical objects of conformational analysis is a state-of-art problem due to specific structural features and their use as the reagents in fine organic synthesis [1–4]. The latter is to a large extent connected with intramolecular rearrangements of carbenium ions formed by protonation of 1,3-dioxanes [5, 6]. A specific place among the six-membered cyclic acetals occupy 5,5-bis(halomethyl)-1,3-dioxanes. This is because of the presence of additional reaction centers, halogen atoms, capable to be involved in nucleophilic substitution reactions. In particular, bis(chloromethyl)analogs are rather easily converted to mono- and diiododerivatives; the process is stereoselective and proceeds predominantly on the equatorial chloromethyl substituent [7].

Conformational behavior of formals of 5,5-bis(halomethyl)-1,3-dioxanes at room temperature is characterized

by fast (in the NMR time scale) ring interconversion [8, 9]. The molecules of their 2-substituted analogs exist predominantly in the *chair* conformation with equatorial substituent at C<sup>2</sup> atom (C<sub>eq</sub>) [10–12]. Also, in recent years, the method of computer modeling of conformational transformations of various molecular systems, in particular, cyclic acetals, is becoming more and more in demand [13]. In view of this, the present work is devoted to investigation of the structure and conformational transformations of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane using <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, X-ray analysis and DFT method (PBE/3ζ) as implemented in PRIRODA software [14].

5,5-Bis(bromomethyl)-2-phenyl-1,3-dioxane was prepared by condensation of 2,2-bis(bromomethyl)-1,3-propanediol with benzaldehyde as described earlier [15] (Scheme 1).

Scheme 1.



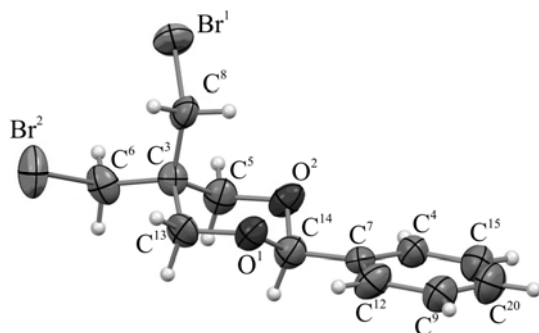
**Table 1.** Crystallographic data and details of X-ray structural experiment

Parameter	Value	Parameter	Value
Empirical formula	C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> Br <sub>2</sub>	<i>F</i> (000)	850.0
<i>M</i>	350.00	Scan region	-10 ≤ <i>h</i> ≤ 8, -10 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 8
<i>T</i> , K	293(2)	Range of reflection indices	2777 ( <i>R</i> <sub>int</sub> 0.0704, <i>R</i> <sub>sigma</sub> 0.1185)
Crystal system	Orthorhombic	Measurements/independent reflections	2777/0/145
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	GOOF	1.039
<i>a</i> , Å	8.2647(7)	<i>R</i> <sub>1</sub> [ <i>I</i> <sub>hkl</sub> > 2σ( <i>I</i> )], <i>wR</i> <sub>2</sub>	<i>R</i> <sub>1</sub> 0.0785, <i>wR</i> <sub>2</sub> 0.1711
<i>b</i> , Å	10.2150(7)	<i>R</i> <sub>1</sub> for <i>I</i> <sub>hkl</sub> , <i>wR</i> <sub>2</sub>	<i>R</i> <sub>1</sub> 0.1330, <i>wR</i> <sub>2</sub> 0.2124
<i>c</i> , Å	14.9449(12)	Δρ <sub>max</sub> /Δρ <sub>min</sub> , e/Å <sup>3</sup>	1.02/-1.12
<i>V</i> , Å <sup>3</sup>	1261.71(17)		
<i>Z</i>	5		
<i>d</i> <sub>calc</sub> , mg/mm <sup>3</sup>	2.290		
μ, mm <sup>-1</sup>	8.009		

**Table 2.** Selected bond distances, bond and dihedral angles in the molecule of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane

Bond	Bond distance, Å		Bond angle	φ, deg		Dihedral angle	φ, deg	
	calculated	experiment		calculated	experiment		calculated	experiment
O <sup>1</sup> -C <sup>13</sup>	1.429	1.402(16)	C <sup>13</sup> O <sup>1</sup> C <sup>14</sup>	110.6	110.6(10)	C <sup>4</sup> C <sup>7</sup> C <sup>14</sup> O <sup>2</sup>	-30.7	-36.4(17)
O <sup>1</sup> -C <sup>14</sup>	1.423	1.432(16)	C <sup>14</sup> O <sup>2</sup> C <sup>5</sup>	110.5	109.4(11)	C <sup>12</sup> C <sup>7</sup> C <sup>14</sup> O <sup>1</sup>	29.6	30.5(16)
O <sup>2</sup> -C <sup>5</sup>	1.430	1.423(16)	O <sup>2</sup> C <sup>14</sup> O <sup>1</sup>	111.2	108.7(11)	C <sup>14</sup> O <sup>1</sup> C <sup>13</sup> C <sup>3</sup>	-59.6	-59.8(13)
O <sup>2</sup> -C <sup>14</sup>	1.423	1.398(15)	O <sup>2</sup> C <sup>5</sup> C <sup>3</sup>	111.3	112.1(10)	O <sup>1</sup> C <sup>13</sup> C <sup>3</sup> C <sup>5</sup>	53.2	53.0(13)
C <sup>7</sup> -C <sup>14</sup>	1.513	1.481(19)	O <sup>1</sup> C <sup>13</sup> C <sup>3</sup>	111.8	110.4(10)	C <sup>14</sup> O <sup>2</sup> C <sup>5</sup> C <sup>3</sup>	58.2	63.2(13)
C <sup>3</sup> -C <sup>6</sup>	1.525	1.509(17)	C <sup>5</sup> C <sup>3</sup> C <sup>13</sup>	105.9	106.3(11)			
C <sup>3</sup> -C <sup>8</sup>	1.529	1.495(17)	C <sup>3</sup> C <sup>6</sup> Br <sup>2</sup>	114.1	114.5(9)			
C <sup>6</sup> -Br <sup>2</sup>	1.989	1.921(15)	C <sup>3</sup> C <sup>8</sup> Br <sup>1</sup>	114.0	113.3(9)			
C <sup>8</sup> -Br <sup>1</sup>	1.987	1.949(12)	C <sup>7</sup> C <sup>14</sup> O <sup>2</sup>	109.6	110.8(12)			

The structure of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane was determined by X-ray analysis; the results have been deposited to the Cambridge Crystallo-

**Fig. 1.** Crystal structure of the molecule of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane.

graphic Data Centre, no. 1558755. Crystallographic details are given in Table 1.

In the crystal, the molecules of 5,5-bis(bromomethyl)-2-phenyl-1,3-dioxane exist in the *chair* conformation with equatorial phenyl group (*C*<sub>eq</sub>, Fig. 1). The planes of the aromatic ring and the O<sup>1</sup>C<sup>13</sup>C<sup>5</sup>O<sup>2</sup> fragment are coplanar. Heteroatomic part of the heterocycle is characterized by typical values of the C–O bond lengths (1.398–1.432 Å) and bond angles close to 110°. Dihedral angles are also close to those typical for the *chair* conformation (Table 2) [2, 10]. Note that bromomethyl substituents are located in the *gauche*-position to each other (Fig. 1); earlier, using quantum-chemical calculations, we have shown that this form corresponds to energy minimum as compared to other conformations of the C–halogen bond in the substituting groups at the C<sup>5</sup> atom of the heterocyclic ring [11].