AM1 Study of Conformations of Oxocane and 1,3-Dioxocane

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Summary. AM1 semi-empirical SCF MO calculations are reported for important conformations of oxocane (**1**) and 1,3-dioxocane (**2**). The boat-chair conformation of **1** (**BC-1**) is found to be the most stable form, whereas the crown family conformation is calculated to be $3.7 \, kJ \cdot mol^{-1}$ less stable. The boat-boat form of **1** is $15.9 \, kJ \cdot mol^{-1}$ less stable than **BC-1**. The boat-chair conformation of **2** (**BC-1,3**) is calculated to be the most stable form of 1,3-Dioxocane. The crown-family conformation and the boat-boat geometry of this compound are 4.2 and $8.3 \, kJ \, mol^{-1}$ less stable than **BC-1,3**.

Keywords. Oxocane; 1,3-Dioxocane; Conformational analysis; Stereochemistry; AM1 calculations.

AM1-Rechnungen zu den Konformationen von Oxocane und 1,3-Dioxocan

Zusammenfassung. Die wesentlichen Konformationen von Oxocan (**1**) und 1,3-Dioxocan (**2**) wurden mittels semiempirischer AM1-Rechnungen (SCF MO) untersucht. Die Wanne-Sessel-Konformation von **1** (**BC-1**) ist am stabilsten; Konformationen aus der Klasse der Kronen sind um $3.7 \, kJ \cdot mol^{-1}$ energiereicher. Die Wanne-Wanne-Konformation von **1** ist um $15.9 \, kJ \cdot mol^{-1}$ instabiler als **BC-1**. Die Wanne-Sessel-Konformation von **2** (**BC-1,3**) ist das stabilste Konformer von 1,3-Dioxocan. Kronen-konformationen und Wanne-Wanne-Geometrien sind um 4.2 und $8.3 \, kJ \cdot mol^{-1}$ energiereicher als **BC-1,3**.

Introduction

There are three families of rapidly pseudorotating conformations in saturated eight-membered rings (Fig. 1). Each family is separated from the other two by substantial barriers of the order of about $40 \, kJ \cdot mol^{-1}$ [1]. In the case of the parent hydrocarbon cyclooctane, the boat-chair (**BC**, about 95%) and a crown-family conformation, most likely the twist-chair-chair (**TCC**, about 5%), are populated at room temperature [2]. The successive replacement of the methylene groups in cyclooctane by oxygen atoms is expected to change the proportions between these two types, but the third family (boat–boat, **BB**) is virtually unpopulated in all cases [3–7]. However, the replacement of a methylene group by an oxygen atom is expected to have significant effects on torsional barriers and internal angles.

The conformational aspects of saturated oxygen heterocyclic rings are of interest because several eight-membered oxygen containing rings are found in
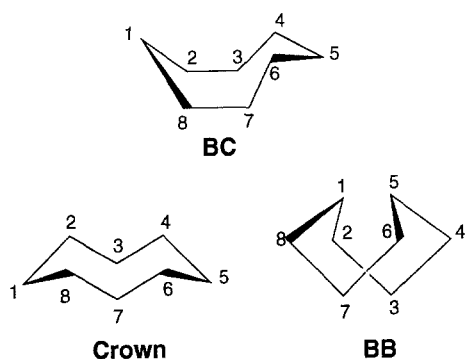
Fig. 1. Important equilibrium geometries of cyclocotane

sesquiterpenoids of marine origin and a few other natural sources [9]. We report here a conformational study of oxocane (oxacyclooctane, 1) and 1,3-dioxocan (2) by Austin Model 1 (AM1) [10] semi-empirical molecular orbital calculations. AM1 is one of the most reliable semi-empirical methods known for calculating various structural aspects of organic molecules.
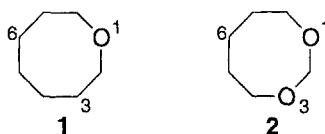
Results and Discussion
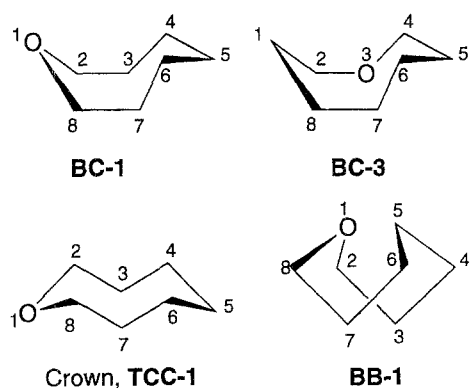
Oxocane (1)

The results of semi-empirical AM1 calculations for various conformations of **1** are shown in Table 1. The replacement of a methylene group by an oxygen atom in the boat-chair conformation of cyclooctane should lead to a large decrease in non-bonded repulsion for positions 1, 3, and 7 (Fig. 2). Thus, the plane symmetrical boat-chair form with an oxygen atom in position 1 (**BC-1**) is calculated to be the most stable geometry. This conformation reduces unfavorable 1,4 transannular nonbonded interactions between the inward pointing hydrogen atoms at these sites in cyclooctane.

The boat-chair conformations with the oxygen atom in position 3 or 7 (**BC-3** or **BC-7**) are the next favorable geometries; they are stabilized by the oxygen being in positions to relieve 1,5 transannular nonbonded interactions. The crown-family conformation, twist-chair-chair (**TCC**), is calculated to be $3.7 \, \mathrm{kJ \cdot mol^{-1}}$ less stable than the ground state conformation. Other boat-chair conformations such as **BC-2** (or **BC-8**), **BC-4** (or **BC-6**) and **BC-5** are calculated to have 4.9, 4.4 and $3.7 \, \mathrm{kJ \cdot mol^{-1}}$ more energy than **BC-1**. The twist-boat-boat (**TBB**) form is calculated to be $15.9 \, \mathrm{kJ \cdot mol^{-1}}$ less stable than **BC-1**. Thus, it is not expected to be significantly populated at room temperature.

Table 1. Heats of formation (kJ·mol^{-1}) and dihedral angles (°) of various forms of oxocane (**1**) and 1,3-dioxocane (**3**)

oxocane (**1**)	BC-1 C_3	BC-2 C_1	BC-3 C_1	BC-4 C_1	BC-5 C_s	TCC C_1	BB-1 C_3	BB-2 C_1
ΔH_f^0	−310.4	−305.5	−307.7	−306.0	−306.7	−306.7	−294.5	−285.4
$\Delta\Delta H_f^0$	0.0	4.9	1.7	4.4	3.7	3.7	15.9	25.0
Dipole moment (D)	1.24	1.52	1.39	1.39	1.45	1.39	1.29	1.57
ϕ_{234}	39	105	67	−70	104	−69	−45	−29
ϕ_{2345}	−102	−69	−65	100	−41	70	47	−69
ϕ_{3456}	74	73	107	−46	−65	−103	50	26
ϕ_{4567}	−74	−98	−51	−64	65	103	−50	70
ϕ_{5678}	102	34	−57	78	41	−70	−47	−29
ϕ_{6781}	−39	74	60	32	104	69	45	−68
ϕ_{7812}	−78	−63	54	−108	78	−112	61	24
ϕ_{8123}	78	−49	113	81	−78	112	−61	74

1,3-dioxocane (**2**)	BC-1,3 C_1	BC-2,4 C_1	BC-3,5 C_1	BC-4,6 C_s	BC-2,8 C_3	TCC C_1	TBB C_1
ΔH_f^0	−470.0	−457.1	−461.2	−457.1	−454.3	−465.8	−461.7
$\Delta\Delta H_f^0$	0.0	12.9	8.8	12.9	15.7	4.2	8.3
Dipole moment (D)	0.45	2.45	2.58	2.35	2.68	2.48	0.27
ϕ_{234}	51	−114	74	−82	72	87	−61
ϕ_{2345}	−115	79	−74	109	38	106	64
ϕ_{3456}	69	−69	106	−37	−99	−96	50
ϕ_{4567}	−68	93	−47	−70	69	77	−50
ϕ_{5678}	101	−34	−57	70	−69	−77	−52
ϕ_{6781}	−45	−72	61	37	99	96	51
ϕ_{7812}	−72	65	53	−109	−38	−105	65
ϕ_{8123}	72	45	−114	82	−72	87	−62

BC-1   BC-3

Crown, TCC-1   BB-1

Fig. 2. Important equilibrium geometries of oxocane (**1**)

1,3-Dioxocane (2)

For 1,3-dioxocane (**2**), the boat-chair conformation with the oxygen atoms in positions 1 and 3 (**BC-1,3** or its mirror image **BC-1,7**) is calculated to be the most stable conformation (Fig. 3) in agreement with NMR and dipole moment results [5, 7]. The replacement of oxygen atoms at positions 1 and 3 (or 1 and 7) leads to a favorable torsional angle arrangement about the O–CH$_2$–O moiety that is almost the same as the one found in dimethoxymethane [14].
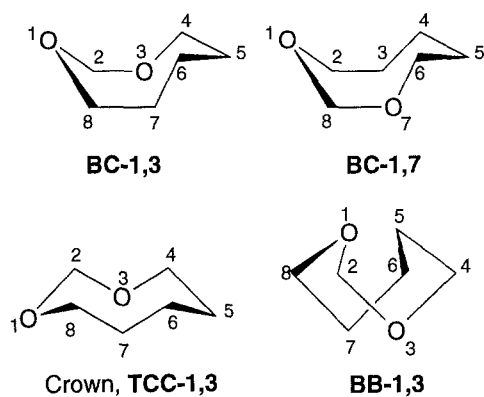
Fig. 3. Important equilibrium geometries of 1,3-di-oxocane (2)

The greater relief of nonbounded strain in the cyclooctane boat-chair conformation as a result of replacing two methylene groups by oxygen atoms is expected to occur if the oxygen atoms are placed either in sites 1 and 3 or in sites 1 and 7. As a result, the **BC-1,3** boat-chair minimizes nonbonded and dipole–dipole repulsions and is favorable for anomeric effects [15]. The crown-family conformation,**TCC**, is calculated to be the next favorable conformation ($\Delta\Delta H_f^0 = 4.2 \, \text{kJ} \cdot \text{mol}^{-1}$). The **BB-1,3** geometry is calculated to be $8.3 \, \text{kJ} \cdot \text{mol}^{-1}$ less stable than the ground-state conformation **BC-1,3** (Table 1). In **BB-1,3**, the oxygen atoms occupy positions to relief 1,5 transannular nonbonded interactions. As a result, **BB-1,3** is the third most stable conformation of 1,3-dioxocane. Other boat-chairs, such as **BC-2,4** and **BC-3,5**, which lack symmetry are 12.9 and $8.8 \, \text{kJ} \cdot \text{mol}^{-1}$ less stable than **BC-1,3**. The two plane-symmetrical boat-chairs (**BC-4,6** and **BC-2,8**) have fairly high calculated strain energies due to the unfavorable dipole–dipole interactions.

The present calculations indicate that oxocane can exist as a mixture of boat-chair and crown conformations. The boat–boat form of oxocane is not expected to be populated to a significant amount at room temperature. 1,3-Dioxocane is expected to be conformationaly more homogeneous with the **BC-1,3** boat-chair form as the most favorable geometry.

Methods

Semi-empirical calculations were carried using the AM1 method in the MOPAC 6.0 program [11, 12] implemented on a VAX 4000–300 computer. The energies reported in this study correspond to the molecules in a hypothetical motionless state at 0 K. However, zero-point energy and vibrational enthalpy effects are expected to be similar for the different geometries of a given molecule. Energy-minimum geometries were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints. We have checked that all conformations obtained in the present work are true local energy minima, as evidenced by the fact that they all are calculated to have 3N-6 real vibrational frequencies [13].

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