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Theoretical Calculation and Conformational Analysis of 3,5,7-Triphenyl-1-oxa-3,5,7-triazacyclooctane

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The energy of various conformers of eight membered ring molecule 3,5,7-triphenyl-1-oxa-3,5,7-triazacyclooctane (**2a**) have been calculated. The calculations were performed for HF/3-21+G(d,p) optimized geometries. The calculated energies indicate that saddle family (SF_1) and crown family (CF) conformers are more stable than both-chair (BC), SF_2 and SF_3 conformers. The results of the calculations provide a clear picture of expected energetic differences in conformers and will be useful in both instruction and synthetic planning.

Key Words: Conformational analysis, 3,5,7-Triphenyl-1-oxa-3,5,7-triazacyclooctane.

INTRODUCTION

Stereochemistry of cyclooctanes derivatives have been subject of numerous studies[1-8]. The boat-chair (BC) and crow are usually as the most stable conformation but, compounds with special substitution patterns or with heteroatoms often exist partially or mainly in crown conformation[9,10]. Replacement of CH_2 group in cyclooctane by heteroatomes such as N, O and S leads to different conformational structures[11-15]. Some experimental data on heterocyclic eight-membered rings that give more information about the barrier to interconversion of possible conformers have been published[10]. An interesting eight membered ring compound which can be considered is 3,5,7-triphenyl-1-oxa-3,5,7-triazacyclooctane. The preparation of this compound and its derivatives with electron realizing substituent on phenyl rings carried out by difficulty. But its derivatives with electron withdrawing substituent on phenyl rings have been reported[16]. In our previous paper, we reported, the synthesis, conformation analysis of 3,7-diaryl-1,5-dioxa-3,7-diazacyclooctane (**1**)[17,18]. The purpose of this study is to provide calculated energy and conformational analysis of 3,5,7-triphenyl-1-oxa-3,5,7-triazacyclooctane (**2**) conformers.

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COMPUTATIONAL METHOD

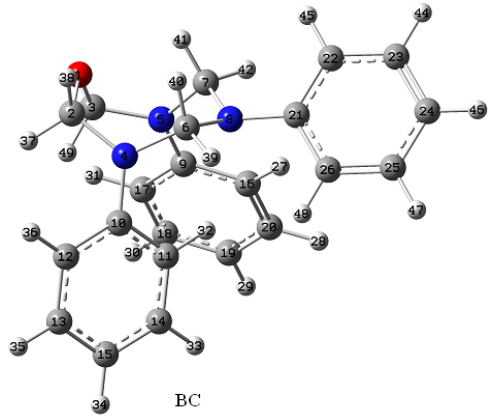
The *ab initio* calculations were carried out using Gaussian 98[19]. All structures were fully optimized using procedures standard to the Gaussian 98 system of computer programs. The Hartree-Fock (HF) theory was employed for the *ab initio* calculations using the HF/3-21+G(d,p) basis set.

RESULTS AND DISCUSSION

ab initio calculations were applied to investigate the conformational analysis of 3,5,7-triphenyl-1-oxa-3,5,7-triazacyclooctane (**2**). For these calculations boat-chair (BC), crown family (CF) and saddle families (SF_1, SF_2 and SF_3) were considered as possible conformers of **2** (Fig. 1). Theoretical calculations show a global minimum for conformer SF_1 (E = -1078.902475) and another one for CF (E = -1078.90160051), which were fully optimized using *ab initio* methods at HF/3-21+g(d,p) level. The calculated energy for different conformations is given in Table-1. The energy differences were also calculated relative to SF_3 as the less stable conformer. These results denote that SF_1 and CF are the most stable conformers, respectively. The calculated energies correctly predict that the saddle family SF_1 is preferred over the BC, CF, SF_2 and SF_3 conformations.

TABLE-1
CALCULATED MINIMUM CONFORMATIONAL ENERGY (E)[a]
CONFORMER FOR 3,5,7-TRIPHENYL-1-OXA-3,5,7-TRIAZACYCLOOCTANE

Conformer	Total energy (au)	ΔE (kcal mol^{-1})	ZPVE
SF_1	-1078.902475	-40.8806	0.446726
CF	-1078.901601	-38.5841	0.445029
BC	-1078.892621	-15.0086	0.445580
SF_2	1078.889185	5.98753	–
SF_3	-1078.886905	0	–



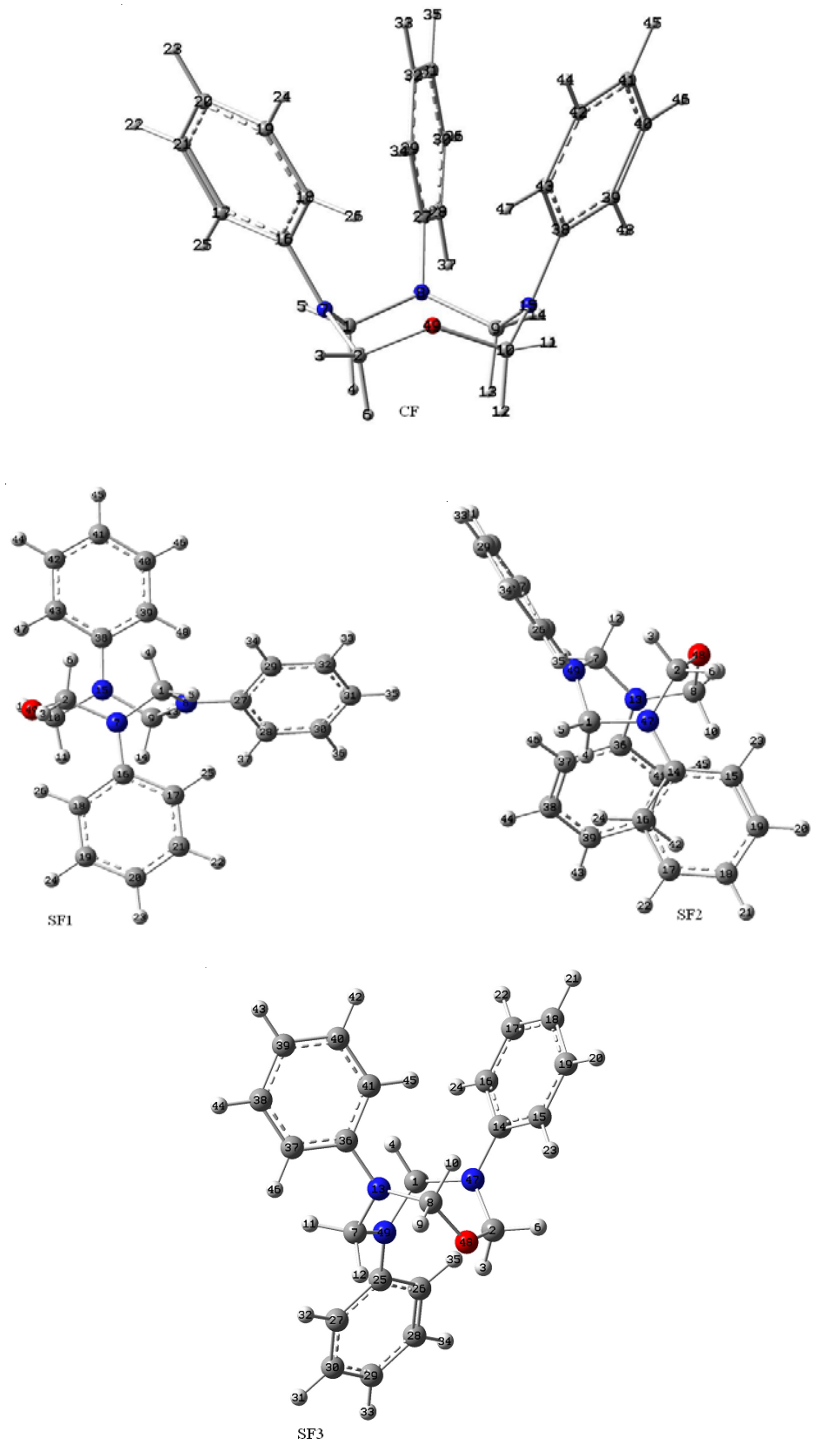


Fig. 1. The most stable conformers BC, CF, SF_1, SF_2 and SF_3

The *ab initio* calculations at HF/3-21+G(d,p) level with zero point vibrational corrected energy (ZPVE) was carried out and torsional angles (ω) as well as other structural properties, bond length and bond angles were measured for previously optimized conformers SF_1 and CF (Tables 2 and 3).

TABLE-2
CALCULATED GEOMETRIES FOR SF_1 CONFORMER
AT HF/3-21+G(d,p) METHOD

Bond length (Å)		Bond angles (º)		Torsion angles (º)	
O(49)-C(10)	1.455	O(49)-C(2)-N(7)	115.1	O(49)-C(2)-N(7)-C(1)	104.0
O(49)-C(2)	1.455	C(2)-N(7)-C(1)	118.1	O(49)-C(10)-N(15)-C(9)	105.1
C(10)-N(15)	1.442	O(49)-C(10)-N(15)	115.1	C(10)-N(15)-C(9)-N(8)	-113.6
C(2)-N(7)	1.442	C(10)-O(49)-C(2)	121.1	N(15)-C(9)-N(8)-C(1)	36.7
N(15)-C(9)	1.458	N(15)-C(9)-N(8)	112.1	C(9)-N(8)-C(1)- N(7)	36.6
N(7)-C(1)	1.458	C(10)-N(15)-C(9)	118.1	N(8)- C(1)-N(7)-C(2)	-113.6
C(9)-N(8)	1.466	C(9)-N(8)-C(1)	118.3	O(49)-C(2)-N(7)-C(16)	-73.1
C(1)-N(8)	1.466	N(7)-C(1)-N(8)	112.1	O(49)-C(10)-N(15)-C(38)	-73.2
C(2)-H(6)	1.076	C(10)-N(15)-C(38)	121.0	N(8)-C(1)- N(7)-C(16)	64.6
C(2)-H(3)	1.077	C(9)-N(15)-C(38)	120.8	N(8)-C(9)-N(15)-C(38)	64.6
C(10)-H(11)	1.076	C(9)-N(8)-C(27)	120.8	C(2)-O(49)-C(10)-H(12)	-153.0
C(10)-H(12)	1.077	C(1)-N(8)-C(27)	120.8	C(2)-O(49)-C(10)-H(11)	90.2
C(9)-H(13)	1.080	C(1)-N(7)-C(16)	120.8	C(10)-O(49)-C(2)-H(3)	-153.1
C(9)-H(14)	1.079	C(2)-N(7)-C(16)	121.0	C(10)-O(49)-C(2)-H(6)	90.1
C(1)-H(5)	1.080	O(49)-C(2)-H(3)	104.0	H(12)-C(10)-N(15)-C(38)	44.7
C(1)-H(4)	1.079	O(49)-C(2)-H(6)	108.1	H(11)-C(10)-N(15)-C(38)	165.6
N(15)-C(38)	1.405	O(49)-C(10)-H(11)	108.1	C(10)-N(15)-C(9)-H(13)	-55.4
N(7)-C(16)	1.405	O(49)-C(10)-H(12)	104.0	C(10)-N(15)-C(9)-H(14)	-173.1
N(8)-C(27)	1.398	N(7)-C(2)-H(3)	111.1	C(27)-N(8)-C(9)-H(13)	-21.8
		N(7)-C(2)-H(6)	108.5	[C(27)-N(8)-C(9)-H(14)	96.7
		N(7)-C(1)-H(4)	107.2	C(27)-N(8)-C(1)-H(5)	96.7
		N(7)-C(1)-H(5)	110.4	C(27)-N(8)-C(1)-H(4)	-21.8
		N(8)-C(1)-H(4)	111.2	C(16)-N(7)-C(1)-H(5)	-173.1
		N(8)-C(1)-H(5)	107.7	C(16)-N(7)-C(1)-H(4)	-55.4
		N(8)-C(9)-H(13	107.7	C(16)-N(7)-C(2)-H(3)	44.7
		N(8)-C(9)-H(14)	111.2	C(16)-N(7)-C(2)-H(6)	165.6
		N(15)-C(9)-H(13)	110.4		
		N(15)-C(9)-H(14)	107.2		
		N(15)-C(10)-H(11)	108.5		
		N(15)-C(10)-H(12)	111.1		

TABLE-3
CALCULATED GEOMETRIES FOR CROWN FAMILY
CONFORMER AT HF/3-21+G(d,p) METHOD

Bond length (Å)		Bond angles (º)		Torsion angles (º)	
O(49)-C(10)	1.456	O(49)-C(2)-N(7)	115.5	O(49)-C(2)-N(7)-C(1)	87.6
O(49)-C(2)	1.456	C(2)-N(7)-C(1)	118.9	O(49)-C(10)-N(15)-C(9)	-84.1
C(10)-N(15)	1.436	O(49)-C(10)-N(15)	115.5	C(10)-N(15)-C(9)-N(8)	88.3
C(2)-N(7)	1.437	C(10)-O(49)-C(2)	119.6	N(15)-C(9)-N(8)-C(1)	-83.3

Bond length (Å)		Bond angles (º)		Torsion angles (º)	
N(15)-C(9)	1.471	N(15)-C(9)-N(8)	116.8	C(9)-N(8)-C(1)- N(7)	77.7
N(7)-C(1)	1.472	C(10)-N(15)-C(9)	118.5	N(8)- C(1)-N(7)-C(2)	-81.2
C(9)-N(8)	1.458	C(9)-N(8)-C(1)	120.0	O(49)-C(2)-N(7)-C(16)	-77.9
C(1)-N(8)	1.458	N(7)-C(1)-N(8)	118.1	O(49)-C(10)-N(15)-C(38)	76.8
C(2)-H(6)	1.083	C(10)-N(15)-C(38)	118.7	N(8)-C(1)- N(7)-C(16)	83.9
C(2)-H(3)	1.076	C(9)-N(15)-C(38)	119.9	N(8)-C(9)-N(15)-C(38)	-72.4
C(10)-H(11)	1.082	C(9)-N(8)-C(27)	118.3	C(2)-O(49)-C(10)-H(12)	-39.1
C(10)-H(12)	1.075	C(1)-N(8)-C(27)	120.5	C(2)-O(49)-C(10)-H(11)	-156.4
C(9)-H(13]	1.081	C(1)-N(7)-C(16)	121.2	C(10)-O(49)-C(2)-H(3)	151.8
C(9)-H(14)	1.076	C(2)-N(7)-C(16)	118.3	C(10)-O(49)-C(2)-H(6)	34.5
C(1)-H(5)	1.075	O(49)-C(2)-H(3)	104.3	H(12)-C(10)-N(15)-C(38)	-161.2
C(1)-H(4)	1.082	O(49)-C(2)-H(6)	108.4	H(11)-C(10)-N(15)-C(38)	-40.7
N(15)-C(38)	1.422	O(49)-C(10)-H(11)	104.3	C(10)-N(15)-C(9)-H(13)	-32.9
N(7)-C(16)	1.420	O(49)-C(10)-H(12)	108.3	C(10)-N(15)-C(9)-H(14)	-149.4
N(8)-C(27)	1.436	N(7)-C(2)-H(3)	109.4	C(27)-N(8)-C(9)-H(13)	-155.0
		N(7)-C(2)-H(6)	108.9	C(27)-N(8)-C(9)-H(14)	-38.3
		N(7)-C(1)-H(4)	106.4	C(27)-N(8)-C(1)-H(5)	33.4
		N(7)-C(1)-H(5)	108.7	C(27)-N(8)-C(1)-H(4)	149.8
		N(8)-C(1)-H(4)	107.5	C(16)-N(7)-C(1)-H(5)	-38.8
		N(8)-C(1)-H(5)	107.4	C(16)-N(7)-C(1)-H(4)	-155.2
		N(8)-C(9)-H(13)	108.2	C(16)-N(7)-C(2)-H(3)	39.4
		N(8)-C(9)-H(14	107.9	C(16)-N(7)-C(2)-H(6)	159.8
		N(15)-C(9)-H(13)	106.8		
		N(15)-C(9)-H(14	108.9		
		N(15)-C(10)-H(11)	108.9		
		N(15)-C(10)-H(12)	108.9		

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