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An *ab initio* Molecular Orbital Study of the Conformational Properties of all-(Z)-Cyclododeca-1,4,7,10-tetraene

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Summary. *Ab initio* HF/6-31G* and MP2/6-31G*//HF/6-31G* methods were used to calculate the structure optimization and conformational interconversion pathways for all-(*Z*)-cyclododeca-1,4,7,10-tetraene. This compound adopts the symmetrical crown (C_{4v}) conformation. Ring inversion takes place *via* symmetrical intermediates, such as boat-chair (*BC*, C_s) and twist (C_{2h}) conformers and requires about 22.3 kJ · mol^{-1}. The calculated strain energies for *BC* and twist conformers are 5.9 and 13.5 kJ · mol^{-1}. The results of semiempirical AM1 calculations for structural parameters and relative energies of the important geometries of the title compound are in good agreement with the results of *ab initio* methods.

Keywords. Medium rings; Stereochemistry; Conformational analysis; Molecular modeling.

Introduction

All-(*Z*)-Cyclododeca-1,4,7,10-tetraene (**1**) has been isolated from the intramolecular cyclization of all-(*Z*)-dodeca-3,6,9-trienedial under *McMurry* conditions [1, 2]. Compound **1** is of special interest as a tetrahomo-8π-system with maximum interaction of all π-bonds which is guaranteed in the crown (C_{4v}) conformation. The X-ray structure analysis of **1** at 120 K [3] confirms the crown conformation in the solid state. The fact that **1**, in contrast to cyclooctatetraene, prefers a conformation in which all double bonds are coplanar, is attributed to the absence of a homo-antiaromatic destabilization [3, 4].

This study was undertaken to investigate the structural optimization and conformational interconversion pathways of the twelve-membered ring by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The results from MP2/6-31G*//HF/6-31G* calculations are used in the conformational energies discussions below.

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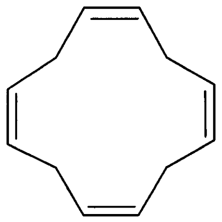

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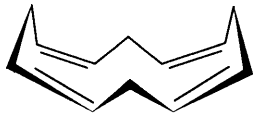

Crown, C_{4v}

Results and Discussion

All-(*Z*)-Cyclododeca-1,4,7,10-tetraene (**1**), with four ethylenic chromophores alternatively inserted in carbon–carbon bonds of cyclobutane, could experience 8π-electron cyclic interactions of the in-plane π bonds of the four ethylenic moieties, and might exhibit homoantiaromaticity [5, 6]. This 'expanded cyclobutane' is expected to manifest special conformational properties, since the torsional strain and transannular *van der Waals* repulsion, which play such a crucial rule in determining the relative energies of the various conformers of cyclobutane, will be greatly reduced [7]. X-Ray crystallographic data [3] obtained for **1** are interpreted in terms of a crown conformation in which all four double-bonds are coplanar.

Five geometries (three energy minima and two transition states) were found to be necessary for a description of the conformational properties of **1**. The most stable conformation of **1** is the crown (C_{4v}) geometry, in agreement with available

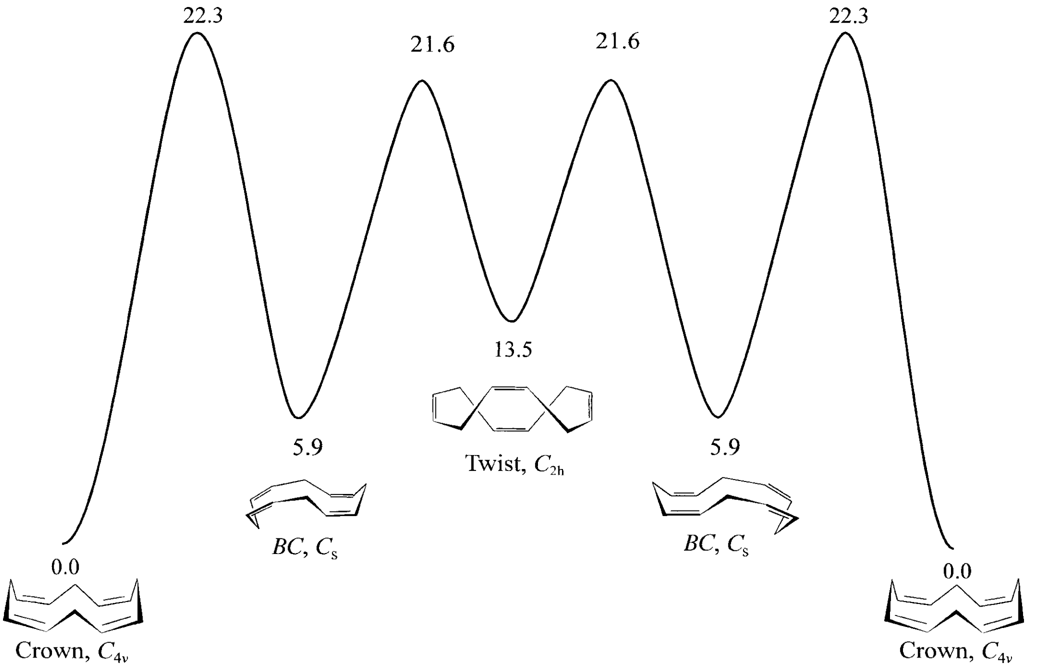

Fig. 1. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ · mol^{-1}) profile for the conformational interconversion of **1**

Table 1. Calculated heats of formation (kJ · mol^{-1}), total and zero-point vibrational[a] energies (*Hartree*), relative energy (including zero-point energy, kJ · mol^{-1}), and structural parameters of **1**

Feature	Crown, C_{4v}			BC, C_s		Twist, C_{2h}		(Crown $\rightleftharpoons$ BC)[b], C_s		(BC $\rightleftharpoons$ Twist)[c], C_1	
	AM1	*ab initio*	X-ray	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH_f°	164.6			170.3		178.4		188.6		203.9	
$\Delta\Delta H_f^\circ$	0.0			5.7		13.8		24.0		39.3	
HF/6-31G*//HF/6-31G*		−463.647559			−463.642134		−463.639565		−465.632839		−463.636492
MP2/6-31G*//HF/6-31G*		−465.172979			−465.170723		−465.167830		−465.164488		−465.164771
ZPE		0.266701			0.266557		0.266034		0.266424		0.266242
E_{rel}^{b}		0.0			13.9		19.4		38.00		28.00
E_{rel}^{c}		0.0			5.9		13.5		22.3		21.6
r_{12}	1.334	1.322	1.323	1.334	1.323	1.332	1.323	1.343	1.325	1.335	1.323
r_{23}	1.485	1.510	1.495	1.485	1.512	1.485	1.518	1.491	1.517	1.480	1.517
r_{34}	1.485	1.512	1.505	1.485	1.512	1.484	1.512	1.485	1.517	1.478	1.505
r_{45}	1.334	1.322	1.321	1.333	1.323	1.334	1.323	1.335	1.325	1.335	1.322
r_{56}	1.485	1.512	1.503	1.485	1.514	1.485	1.512	1.487	1.515	1.482	1.520
r_{67}	1.485	1.512	1.506	1.485	1.510	1.487	1.518	1.486	1.515	1.489	1.520
r_{78}	1.334	1.322	1.325	1.333	1.323	1.333	1.323	1.334	1.323	1.333	1.322
r_{89}	1.494	1.512	1.507	1.484	1.523	1.485	1.518	1.485	1.505	1.485	1.511
r_{910}	1.485	1.512	1.501	1.485	1.512	1.484	1.512	1.495	1.505	1.483	1.515
r_{1011}	1.334	1.320	1.326	1.332	1.323	1.334	1.323	1.342	1.323	1.338	1.321
r_{1112}	1.485	1.510	1.503	1.485	1.514	1.485	1.512	1.476	1.525	1.488	1.511
r_{121}	1.485	1.520	1.506	1.484	1.514	1.486	1.518	1.476	1.515	1.480	1.513
θ_{234}	111.1	111.2	110.8	113.1	111.8	113.5	114.3	112.9	110.7	126.1	117.5
θ_{345}	127.2	128.3	127.5	126.2	127.9	126.2	127.7	128.8	130.3	132.9	127.7
θ_{456}	127.2	128.3	126.8	127.3	127.9	126.3	127.7	128.7	129.8	128.8	128.3
θ_{567}	111.3	111.2	112.0	111.4	114.8	113.5	114.3	110.2	113.6	108.8	119.7
θ_{678}	127.2	128.3	127.7	127.3	127.4	125.8	127.7	128.9	123.6	126.8	130.2

(*continued*)

Table 1 (*continued*)

Feature	Crown, C_{4v}			BC, C_s		Twist, C_{2h}		(Crown $\rightleftharpoons$ BC)[b], C_s		(BC $\rightleftharpoons$ Twist)[c], C_1	
	AM1	*ab initio*	X-ray	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
θ_{789}	127.2	128.3	127.2	126.2	126.8	125.8	127.7	128.8	120.5	126.3	129.2
θ_{8910}	111.3	111.2	110.3	113.1	113.5	113.5	114.3	112.8	120.8	112.2	111.1
θ_{91011}	127.2	128.3	127.3	126.2	126.8	126.1	127.7	123.1	120.6	125.4	127.5
θ_{101112}	127.2	128.3	127.5	127.1	127.4	126.2	127.7	117.9	123.6	125.4	127.0
θ_{11121}	111.3	111.2	111.7	111.4	114.8	113.5	114.3	121.9	113.6	110.7	111.2
θ_{1212}	127.2	128.3	127.1	127.2	127.9	125.8	127.7	118.2	129.8	130.4	130.0
ϕ_{1234}	−118.1	−116.2	117.0	−65.4	−63.3	−65.2	−59.7	−65.2	123.8	37.4	26.9
ϕ_{2345}	118.1	116.2	117.0	127.2	125.3	141.3	138.4	127.1	−123.8	44.0	−128.2
ϕ_{3456}	0.0	0.0	1.9	0.0	1.3	0.0	0.0	0.0	−1.3	−11.1	−0.9
ϕ_{4567}	−118.1	−116.2	117.0	−110.4	−109.4	−141.3	−138.4	−110.3	110.9	−120.4	55.6
ϕ_{5678}	118.1	116.2	117.0	110.3	109.4	65.4	59.7	110.3	−74.3	130.9	45.8
ϕ_{6789}	0.0	0.0	1.9	1.0	1.3	−5.0	−0.7	1.0	2.2	2.5	−2.6
ϕ_{78910}	−118.1	−116.2	117.0	−127.3	−125.3	65.2	59.8	−127.2	−171.8	−121.2	−135.1
ϕ_{891011}	118.1	116.2	117.0	65.2	63.4	−141.4	−138.5	65.1	171.8	68.5	97.6
$\phi_{9101112}$	0.0	0.0	1.9	−4.0	−2.8	0.0	0.0	−4.0	−2.2	−0.7	0.6
$\phi_{1011121}$	−118.1	116.2	117.0	116.1	113.5	141.4	138.5	116.4	74.3	82.4	−109.6
ϕ_{111212}	118.1	116.2	117.0	−116.1	−113.5	−65.3	−59.8	−116.4	−111.0	−154.2	109.2
ϕ_{12123}	0.0	0.0	1.9	4.0	2.8	5.0	0.7	−4.0	1.3	−8.9	−0.3

[a] Zero-point vibrational energy is scaled by a factor of 0.9135 to eleminate known systematic errors in calculations; [b] relative energy with respect to the most stable conformation from HF/6-31G*//HF/6-31G* calculations; [c] relative energy with respect to the most stable conformation from MP2/6-31G*//HF/6-31G* calculations

experimental data [3]. The calculated energy for the second energy minimum, the plane-symmetrical boat-chair (BC, C_s), is $5.9\,\mathrm{kJ \cdot mol^{-1}}$ above that of the crown. Crown and boat-chair conformations are important because they are expected to be significantly populated at room temperature. As the twist (C_{2h}) form is by $13.5\,\mathrm{kJ \cdot mol^{-1}}$ higher in energy than the crown conformation, it is not expected to be significantly populated at ambient temperature unless the calculations are rather seriously erroneous (see Fig. 1 and Table 1).

The simplest conformational process and that with the lowest barrier is the degenerate interconversion of the crown conformation with itself *via* symmetrical intermediates such as boat-chair and twist (Fig. 1). If this process is fast, the time-averaged symmetry of the crown conformation becomes D_{4h}, which is the maximum symmetry allowed by the constitution of **1**.

Having found the conformational transition states and intermediates for the ring inversion of **1**, it is still necessary to determine whether the potential energy surface affords the lowest path. Since the potential energy surface is highly multidimensional, it is not possible to explore all possibilities, but we have carried out a sufficient amount of calculations to feel confident that the lowest path, or something close to it, was obtained.

Selected data for various geometries of **1** are given in Table 1. A comparison of bond lengths and bond angles shows fairly small differences. The internal angles are close to the unstrained values in energy-minimum conformations, but are expanded in transition-state geometries.

In summary, HF/6-31G* calculations provide a picture of the conformations of **1** from both structural and dynamic points of view. Compound **1** is predicted to exist as a mixture of two symmetrical conformations, crown (C_{4v}) and boat-chair (C_s). Ring inversion in **1** takes place *via* boat-chair and twist (C_{2h}) intermediates and requires about $22.3\,\mathrm{kJ \cdot mol^{-1}}$.

Methods

An initial estimate of the geometry of **1** was obtained by the molecular mechanics program PCMODEL (88.0) [8] followed by full minimization using the semiempirical AM1 method [9] in the MOPAC 6.0 [10, 11] computer program implemented on a VAX 4000–300 computer. Optimal geometries were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of *Dewar et al.* [12] (keyword SADDLE). All geometries were characterized as stationary points. True local energy minima and transition states on the potential energy surface were found using the keyword FORCE. All energy-minimum and transition-state geometries obtained in this work were calculated to have 3*N*-6 and 3*N*-7 real vibrational frequencies, respectively [13, 14].

The AM1 results were used as input for the *ab initio* calculations which were carried out using the GAUSSIAN 98 [15] program. The geometries of all structures were fully optimized by means of analytical energy gradients using the *Berny* optimizer without geometrical constraints [16, 17]. The restricted *Hartree-Fock* calculations with the split-valence 6-31G* basis set, which include a set of d-type polarization functions on all non-hydrogen atoms, were used in these calculations [18]. Single point energy calculations at the MP2/6-31G*//HF6-31G* level were used to evaluate the electron correlation effects in the energies and order of stability of conformers. Vibrational frequencies were calculated at the 6-31G* level for all minimum energies and transition states, which were confirmed to have zero and one imaginary frequency, respectively. The frequencies were scaled by a factor of 0.91 [19] and used to compute the zero-point vibrational energies.

References

[1] Brudermüller M, Musso H (1988) Angew Chem Int Ed Engl **27**: 298
[2] McMurry JE, Flamming MP, Kees KL, Krepski LP (1978) J Org Chem **43**: 3255
[3] Krause A, Musso H, Boland W, Ahlrichs R, Gleiter R, Boese R, Bar M (1989) Angew Chem Int Ed Engl **28**: 1379
[4] Wilcox CF, Blain DA, Clardy J, Van Duyne G, Gleiter R, Eckert-Maksic M (1986) J Am Chem Soc **108**: 7693
[5] Warner PM (1977) In: Topics in Nonbenzenoid Aromatic Chemistry, vol 2. Hirokawa Publishing Co Tokyo
[6] Paquette LA (1978) Angew Chem Int Ed Engl **17**: 106
[7] Egawa T, Fukuyama T, Yamamoto S, Takabagashi F, Kambara H, Ueda T, Kuch-itsu K (1997) J Chem Phys **86**: 6018
[8] PCMODEL (88.0) Serena Software, Box 3976, Bloomington, IN, USA
[9] Dewar MJS, Zeobisch EG, Healy EF, Stewart JJP (1985) J Am Chem Soc **107**: 3902
[10] Stewart JJP, QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN, USA
[11] Stewart JJP (1990) J Comput Aided Mol Des **4**: 1
[12] Dewar MJS, Healy EF, Stewart JJP (1984) J Chem Soc Faraday Trans **80**: 227
[13] McIver JW Jr (1974) Acc Chem Res **7**: 72
[14] Ermer O (1975) Tetrahedron **31**: 1849
[15] Frisch MJ et al (1998) Gaussian 98, Revision A 6. Gaussian Inc Pittsburgh PA
[16] Jensen F (1999) Introduction to Computational Chemistry. Wiley, New York
[17] Hehre W, Radom L, Schleyer PVR, Pople JA (1986) Ab Initio Molecular Orbital Theory. Wiley, New York
[18] Hariharan PC, Pople JA (1973) Theor Chim Acta **28**: 213
[19] Grev RS, Janssen CL, Schaefer HF (1991) Chem Phys **95**: 5128

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