SHORT PAPER

J. Chem. Research (S), 2002, 124–127

Conformations of all-*trans*-cyclododeca-1,4,7,10-tetraene[†]

Issa Yavari[a]*, Manzarbanoo Esnaashari[b] and Mehdi Adib[a]

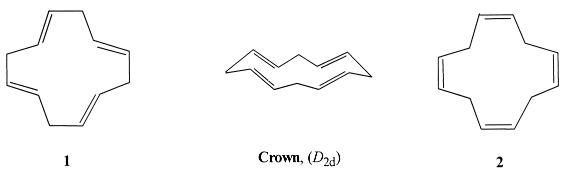
[a] *Department of Chemistry, University of Tarbiat Modaress, PO Box 14155-4838, Tehran, Iran*
[b] *Department of Chemistry, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran*

Ab initio HF/6-31G* and MP2/6-31G*//HF/6-31G* methods were used to calculate the relative energies of the important energy-minimum conformations and transition-state geometries of all-*trans*-cyclododeca-1,4,7,1 0-tetraene; the calculated energy-barrier for ring inversion of the crown (D_{2d}) conformation is 36.1 kJ/mol.

Keywords: conformational energy, *ab initio* molecular orbital, molecular modelling, cyclic tetraenes

Introduction

All-*trans*-cyclododeca-1,4,7,10-tetraene (**1**), with four ethylenic chromophores alternatively inserted in the 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.[1,2] Although, the synthesis[3,4] and structural[5] properties of all-*cis*-cyclododeca-1,4,7.10-tetraene (**2**) have been the subject of several important investigations, the extent of our knowledge concerning the synthesis and conformations of the less stable all-*trans*-isomer **1** is meagre. Compound (**1**) is of special interest as a tetrahomo-8π-system, when all four π-bonds are so arranged that maximum interaction is guaranteed. This arrangement is realised with the symmetrical crown (D_{2d}) conformation. This ‘expanded cyclobutane’ is expected to manifest special conformational properties, since the torsional strain and transannular van der Waals repulsions, which play such a crucial rule in determining the relative energies of the various conformers of medium rings, will be greatly reduced.[6,7] This study was undertaken to investigate the structural optimisation and conformational inter-conversion pathways of the cyclododecatetraene **1** by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The



Scheme 1

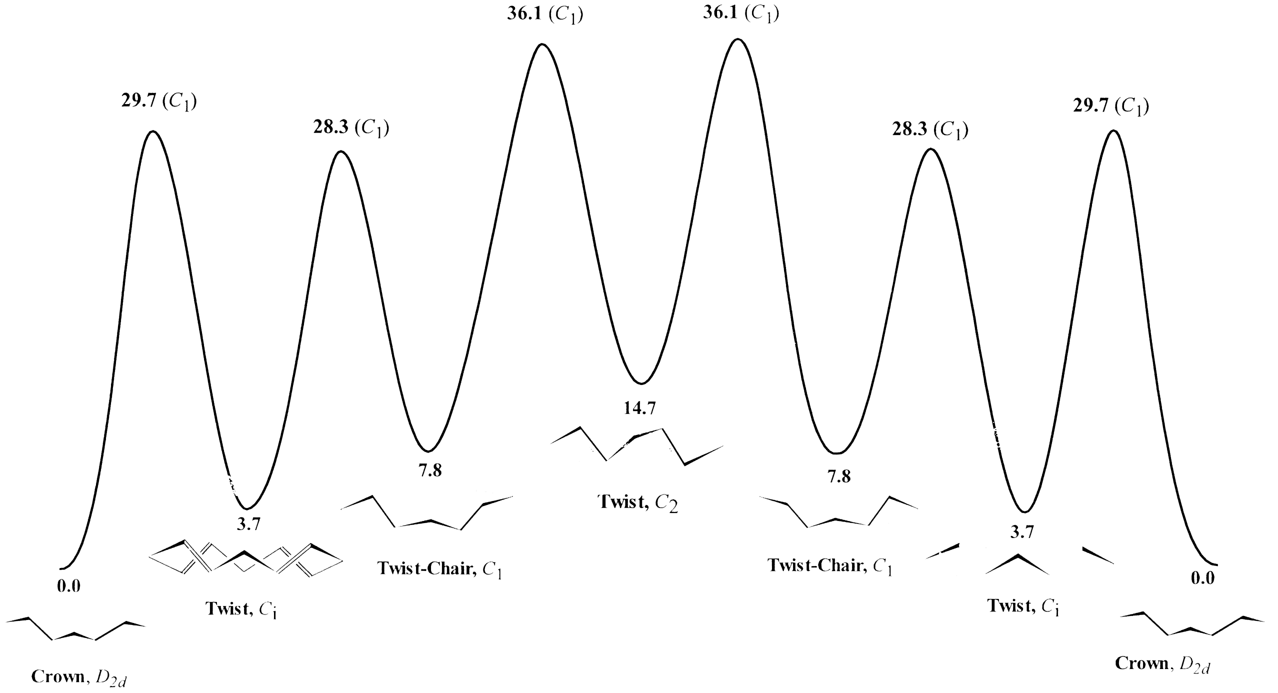


Fig.1 Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ/mol) profile for ring inversion of all-*trans*-cyclododeca-1,4,7,10-tetraene **(1)**

---

* To receive any correspondence. E-mail: isayavar@yahoo.com

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

results of MP2/6-31G*//HF/6-31G* calculations are used in the conformational energies discussions below.

Results and discussion

Altogether seven geometries were found important for a description of the conformational features of all-*trans*-cyclododeca-l,4,7,10-tetraene (**1**). Four of these geometries correspond to energy minima and three are one-dimensional energy maxima (saddle points or transition states) as shown in Fig. 1 and Tables l and 2. Based on the relative orientations of the double bonds in compound **1**, the three energy-minimum conformations can be classified as parallel–parallel, parallel–crossed, and crossed–crossed (see Fig. 1). The most stable conformation of **1** is the symmetrical crown (D_{2d}) geometry of the parallel–parallel family, which is 7.8 kJ/mol more stable than the best conformer (twist-chair, **TC,** C_1) of the parallel–crossed family. The most stable conformation of the crossed–crossed family is the C_1-symmetric twist[8] form which is 3.7 kJ/mol less stable than the global energy-minimum conformation. The C_2-symmetric twist geometry of the crossed–crossed family is calculated to be 14.7 kJ/mol less stable than the crown conformation. Conformations crown, twist *(C_1)*, and twist-chair are important because they are expected to be significantly populated at room temperature. As the axial symmetrical twist form is 14.7 kJ/mol 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).

The simplest conformational process, and the one with the lowest barrier, is the degenerate interconversion of the crown conformation with itself *via* intermediates such as twist *(C_1)*, twist-chair and twist (C_2) geometries (Fig. 1). If this process is

Table 1 Calculated heats of formation (/kJ/mol), total and zero-point vibrational[a] energies (Hartree), relative energy (including zero-point energy/kJ/mol) and structural parameters of energy-minimum conformations of all-*trans*-cyclododeca-1,4,7,10-tetraene **(1)**

Feature	**Crown, D_{2d}**		**Twist, C_i**		**Twist-Chair, C_1**		**Twist, C_2**	
	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH_f°	202.7		202.9		202.1		199.6	
$\Delta\Delta H_f^\circ$	0.6		0.8		0.0		2.5	
HF/6-31G*//HF/6-31G*		–463.633091		–463.631034		–463.629746		–463.625779
MP2/6-31G*//HFI6-31G*		–465.165137		–465.163737		–465.162187		–465.159054
ZPE		0.264737		0.264522		0.264369		0.264765
E_{rel}[b]		0.0		4.9		7.9		19.3
E_{rel}[C]		0.0		3.7		7.8		14.7
r_{12}	1.336	1.319	1.337	1.319	1.336	1.323	1.337	1.320
r_{23}	1.494	1.516	1.493	1.516	1.493	1.512	1.494	1.528
r_{34}	1.494	1.516	1.493	1.516	1.492	1.512	1.490	1.518
r_{45}	1.336	1.319	1.337	1.319	1.337	1.323	1.337	1.320
r_{56}	1.494	1.516	1.493	1.519	1.494	1.514	1.494	1.517
r_{67}	1.494	1.516	1.493	1.519	1.492	1.510	1.490	1.514
r_{78}	1.336	1.319	1.337	1.319	1.337	1.323	1.337	1.320
r_{89}	1.494	1.516	1.493	1.516	1.494	1.523	1.494	1.528
r_{910}	1.494	1.516	1.493	1.516	1.492	1.512	1.490	1.518
r_{1011}	1.336	1.319	1.337	1.319	1.336	1.323	1.337	1.320
r_{1112}	1.494	1.516	1.493	1.519	1.494	1.514	1.494	1.517
r_{121}	1.494	1.516	1.493	1.519	1.492	1.514	1.490	1.514
θ_{123}	123.2	124.6	123.1	126.3	123.0	124.9	122.2	124.0
θ_{234}	105.4	105.5	105.8	105.2	105.5	111.8	107.5	111.7
θ_{345}	123.2	124.6	123.3	126.2	123.7	123.9	124.3	122.7
θ_{456}	123.2	124.6	123.1	122.9	122.5	123.9	122.3	125.6
θ_{567}	105.4	105.5	105.9	107.8	106.1	106.3	107.4	103.9
θ_{678}	123.2	124.6	123.3	122.8	123.8	123.4	124.3	127.9
θ_{789}	123.2	124.6	123.2	126.3	122.5	123.4	122.3	124.0
θ_{8910}	105.4	105.5	105.8	105.2	106.6	106.3	107.4	111.7
θ_{91011}	123.2	124.6	123.1	126.2	123.9	123.9	124.3	122.7
θ_{101112}	123.2	124.6	123.2	122.8	122.6	123.9	122.3	125.6
θ_{11121}	105.4	105.5	105.7	107.8	106.1	106.4	107.4	103.9
θ_{1212}	123.2	124.6	123.3	122.8	123.6	123.9	124.3	127.9
ϕ_{1234}	–160.3	–158.1	–160.8	–159.8	–161.2	–161.8	164.1	162.3
ϕ_{2345}	93.4	96.7	91.8	84.4	93.8	93.7	–55.0	–26.8
ϕ_{3456}	–93.4	–96.7	–93.7	83.9	–95.5	–93.7	–87.0	–76.5
ϕ_{4567}	160.3	158.1	161.1	–159.7	161.0	161.4	164.0	158.8
ϕ_{5678}	–93.4	–96.7	–77.6	88.6	–67.5	–68.4	–55.6	–84.4
ϕ_{6789}	93.4	96.7	–79.4	–88.1	–83.1	–82.4	–87.7	–98.5
ϕ_{78910}	–160.3	–158.1	161.1	159.8	161.9	161.8	164.1	162.3
ϕ_{891011}	93.4	96.7	–92.6	–84.4	–65.1	–68.5	–55.6	–27.0
$\phi_{9101112}$	–93.4	–96.7	92.9		–84.1	–83.5		–76.5
$\phi_{1011121}$	160.3	158.1	–160.9	159.7	162.4	162.2	164.0	158.8
ϕ_{111212}	–93.4	–96.7	78.8	–88.6	–81.5	–82.3	–55.4	–84.4
ϕ_{12123}	93.4	96.7	79.3	88.1	101.5	102.1	–88.3	–98.6

[a] Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculation.

[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.

fast the time-averaged symmetry of the crown conformation becomes D_{4h}, which is the maximum symmetry allowed by the chemical structure of **1**.

Interconversion of the crossed–crossed and parallel–crossed families of **1** can take place by swivelling of one of the double bonds through the unsaturated bridge.[9] Thus, the twist (C_1) conformer can be converted into the twist-chair form *via* a sterically congested unsymmetrical transition state. The calculated strain energy[10] for this process is 28.3 kJ/mol. The swivelling barrier for interconversion of the twist-chair and twist conformers is 36.1 kJ/mol above the crown conformation.

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

Selected geometrical data for various geometries of **1** are given in Table 1. The 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 fairly deformed in the swivelling part of the molecule.

In summary, HF/6-31G* calculations provide a picture of conformations of all-*trans*-cyclododeca-1,4,7,10-tetraene (**1**) from both structural and dynamic points of view. Compound **1** is predicted to exist as a mixture of three conformations, namely crown (D_{2d}), twist (C_1) and twist-chair (C_1). Ring inversion in **1** takes place via twist (C_i), twist-chair and twist (C_2) intermediates and requires about 36.1 kJ/mol. It would be valuable, of course, to have direct structural data on **1** for comparison with the results of the *ab initio* calculations.

Table 2 Calculated heats of formation (kJ/mol), total and zero-point vibrationala energies (Hartree), relative energy (including zero-point energy kJ/mol) and structural parameters of transition-state geometries of all-*trans*-cyclododeca- tetraene **(1)**

Feature	**(Crown=Twist, C_i)$^\#$, C_1**		**(Twist, C_i =TC)$^\#$, C_1**		**(TC=Twist, C_2)$^\#$, C_l**	
	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH_f°	232.2		224.9		227.7	
$\Delta\Delta H_f^\circ$	30.1		22.8		25.6	
HF/6-31G*//HF/6-31G*		−463.618326		−463.618912		−463.615774
MP2/6-31G*//HF/6-31G*		−465.153822		−465.153576		−465.151393
ZPE		0.264661		0.264662		0.264727
E_{rel}[b]		38.6		37.1		45.5
E_{rel}[c]		29.7		28.3		36.1
r_{12}	1.338	1.321	1.337	1.319	1.333	1.319
r_{23}	1.497	1.529	1.493	1.531	1.501	1.536
r_{34}	1.493	1.521	1.493	1.513	1.491	1.514
r_{45}	1.333	1.321	1.337	1.321	1.339	1.322
r_{56}	1.496	1.522	1.493	1.518	1.493	1.522
r_{67}	1.490	1.514	1.493	1.521	1.490	1.517
r_{78}	1.337	1.321	1.337	1.321	1.337	1.319
r_{89}	1.493	1.521	1.493	1.524	1.499	1.534
r_{910}	1.493	1.525	1.493	1.515	1.490	1.514
r_{1011}	1.338	1.321	1.337	1.321	1.341	1.320
r_{1112}	1.493	1.521	1.493	1.525	1.502	1.520
r_{121}	1.494	1.518	1.493	1.526	1.489	1.525
θ_{123}	120.3	123.1	123.1	124.8	119.1	120.5
θ_{234}	105.5	105.6	105.8	107.9	111.4	111.4
θ_{345}	131.0	125.1	123.3	124.3	125.6	125.2
θ_{456}	123.0	122.1	123.1	125.9	122.7	124.6
θ_{567}	114.7	104.1	105.9	103.5	109.5	106.1
θ_{678}	123.6	134.6	123.3	126.9	124.1	128.3
θ_{789}	125.9	121.3	123.2	120.4	123.5	124.4
θ_{8910}	106.1	112.8	105.8	105.5	106.2	109.8
θ_{91011}	122.8	124.1	123.1	134.2	125.4	124.2
θ_{101112}	124.6	125.8	123.2	120.9	119.5	122.6
θ_{11121}	103.1	106.9	105.7	111.9	105.2	67.7
θ_{1212}	123.8	127.3	123.3	125.3	134.2	134.7
ϕ_{1234}	144.9	162.3	−160.8	−162.1	178.5	−177.1
ϕ_{2345}	−70.8	−77.4	91.8	102.7	12.0	28.1
ϕ_{3456}	179.5	100.8	−93.7	−95.8	−104.1	−89.6
ϕ_{4567}	174.0	−148.1	161.1	160.5	166.4	159.0
ϕ_{5678}	−9.5	75.2	−77.6	−79.2	−52.2	−77.0
ϕ_{6789}	61.9	174.1	−79.4	−82.6	−85.2	−101.9
ϕ_{78910}	−163.7	174.5	161.1	148.2	167.1	164.8
ϕ_{891011}	105.8	14.6	−92.6	−64.1	−64.6	−32.8
$\phi_{9101112}$	71.1	−83.0	92.9	−173.8	−87.8	−85.2
$\phi_{1011121}$	−159.3	161.4	−160.9	−175.5	149.5	149.7
ϕ_{111212}	92.2	−82.1	78.8	−13.2	−54.2	−76.3
ϕ_{12123}	−101.1	−92.1	79.3	92.6	−166.7	−172.3

[a] Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculation.
[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.

Computational details

Semiempirical calculations were carried out using the AM1 method[11] with the MOPAC 6.0 program package.[12,13] Energy-minimum geometries were located by minimising energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The geometries of the transition states for conformational interconversion of the equilibrium structures were obtained using the optimised geometries of the equilibrium structures according to procedure of Dewar *et al.*[14] (Keyword SADDLE).

The AM1 results were used as input for the *ab initio* molecular orbital calculations, which were carried out using the GAUSSIAN 98 program.[15] Geometries for all structures were fully optimised by means of analytical energy gradients by Berny optimiser with no geometrical constraints.[16] The restricted Hartree–Fock calculations with the split-valence 6-31G* basis set which include a set of *d*-type polarisation functions on all non-hydrogen atoms were used in these calculations.[17] Single point energy calculations at MP2/6-31G*//HF6-31G* level were used to evaluate the electron correlation effect 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[18] and used to compute the zero-point vibrational energies.

Theoretical calculations provide energy differences and structural parameters for isolated molecules at 0 K. Therefore, theoretical calculations are not expected, in principle, to reproduce the experimental values quantitatively.[19] Nevertheless, it is possible to carry out *ab initio* calculations at the Hartree–Fock level, from which many properties and structural features can be obtained with an accuracy that is competitive with experiment.[20-22] Since the theoretical results are free from intermolecular interferences, they are a valuable tool for a systematic study of conformational effects in simple organic molecules.

Received 30 April 2001; accepted 9 September 2001
Paper 01/853

References

1 L.A. Paquette, *Angew. Chem. Int. Ed. Engl.,* 1978, **17**, 106.
2 T. Egawa, T. Fukuyama, S. Yamamoto, F. Takabagashi, H. Kambara, T. Ueda and K. Kuch-itsu, *J Chem. Phys.,* 1997, **86**, 6018.
3 M. Brudermuller and H. Musso, *Angew. Chem. Int. Ed. Engl.,* 1988, **27**, 298.
4 S. Guiard, M. Santelli and J.-L. Parrain, *Synlett,* 2001, 553.
5 A. Krause, H. Musso, W. Boland, R. Ahlrichs, R. Gleiter, R. Boese and M. Bar, *Angew. Chem. Int. Ed. Engl.,* 1989, **28**, 1379.
6 R. Gleiter and R. Merger, *Tetrahedron Lett.,* 1990, **31**, 1845.
7 C.F. Wilcox, D.A. Blain, J. Clardy, G. Van Duyne, R. Gleiter and M. Eckert-Maksic, *J. Am. Chem. Soc.,* 1986, **108**, 7693.
8 We are grateful to a referee of this paper for suggesting the *C*i-symmetric twist form.
9 E.L. Eliel and S.H. Wilen, *Stereochemistry of Organic Compounds,* Wiley-Interscience, New York, 1994, pp. 1172-1175.
10 E.M. Arnett, J.C. Sanda, J.M. Bollinger and M. Barber, *J. Am. Chem. Soc.,* 1967, **89**, 5389.
11 M.J.S. Dewar, E.G. Zeobisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.,* 1985, **107**, 3902.
12 J.J.P. Stewart, *QCPE* 581, Department of Chemistry, Indiana University, Bloomington, IN, USA.
13 J.J.P. Stewart, *J Comput. Aided Mol. Des.,* 1990, **4**, 1.
14 M.J.S. Dewar, E.F. Healy and J.J.P. Stewart, *J. Chem. Soc., Farady Trans.,* 1984, **80**, 227.
15 Gaussian 98, Revision A. 6, M.J. Frisch, G.W. Ttucks, H.B. Schlegel, G.E. Scuseria M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Startmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rubuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Oritz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J.A. Pople, Gaussian. Inc., Pittsburgh PA, 1998.
16 F. Jensen, *Introduction to Computational Chemistry,* Wiley, New York, 1999; W. Hehre, L. Radom, P. v. R. Schleyer and J.A. Pople, *Ab Initio Molecular Orbital Theory,* Wiley, New York, 1986.
17 P.C. Hariharan and J.A. Pople, *Theor. Chem. Acta,* 1973, **28**,213.
18 R.S. Grev, C.L. Janssen and H.F. Schaefer, *J. Chem. Phys.,* 1991, **95**, 5128.
19 F. Freeman, A. Phornvoranunt and W.J. Hehre, *J. Phys. Org. Chem.,* 1998, **11**, 831.
20 T.M. Gilbert, *Tetrahedron Lett.,* 1998, **39**, 9147.
21 M. Remko, P.D. Lyne and W.G. Richards, *Phys. Chem. Chem. Phys.,* 1999, **1**, 5353.
22 A.D. Strickland and R.A. Caldwell, *J. Phys. Chem.,* 1993, **97**, 13394.