

Table 1 Calculated energies (in Hartree) in various configurations of **2**

Geometry	HF/6-31G*			MP2/6-31G**/HF/6-31G*			B3LYP/6-31G**/HF/6-31G*		
	ZPE ^c	E _{el}	E ₀	E _{el}	E ₀	ΔE ^a	E _{el}	E ₀	ΔE ^a
E-RSS,C ₁	0.1441795	-420.9564064	-420.8122269	0.0381078 (23.9130256) ^d	-422.3361267	0.0269582 (16.9165401) ^d	-423.4787143	0.0279032 (17.5095370) ^d	
Z-RRR,C ₂	0.1442115	-420.9856077	-420.8413962	0.0089385 (5.6089981)	-422.3516661	0.0114188 (7.1654112)	-423.7661742	0.0104433 (6.5532752)	
Z-RSS,C ₁	0.1439183	-420.9894883	-420.84557	0.0047647 (2.9898969)	-422.3563918	0.0066931 (4.1999872)	-423.7681455	0.0084720 (5.3162647)	
E-RRR,C ₁	0.1439694	-420.9646546	-420.8206852	0.0296495 (18.6053578)	-422.3391931	0.0238918 (14.9923434)	-423.7492146	0.0274029 (17.1955938)	
E-RRR,C ₂	0.1430943	-420.9599635	-420.8168692	0.0038160 ^b (2.3945782) ^b	-422.332391	0.0068021 ^b (4.2683858) ^b	-423.7425292	0.0066854 ^b (4.1951554) ^b	
E-RSR,C ₂	0.1436186	-420.9473449	-420.8037263	0.0466084 (29.24723708)	-422.3249832	0.0381017 (23.9091978)	-423.7392790	0.0373385 (23.4302821)	
Z-RSR,C ₂	0.1444910	-420.9948257	-420.8503347	0.0000000 (0.0000000)	-422.3630849	0.0000000 (0.0000000)	-423.7766175	0.0000000 (0.0000000)	

^aRelative to the best configuration.^bRelative to the E-RRR,C₁ conformation.^cCorrected by multiplex by a scaling factor (0.9135).^dNumbers in parenthesis are the corresponding ΔE values in kcal/mol.

As compound **2** has not yet been synthesised, the structural and energetic properties of this compound along with its six possible configurations were investigated computationally using *ab initio* and DFT calculations.

Calculations

Ab initio calculations were carried out using HF/6-31G* level of theory with the GAUSSIAN 98 package programs [6] implemented on a pentium-PC computer with a 300 MHz processor. Initial structural geometries of the compound **2** were obtained by a molecular mechanic program PCMODEL(88.0) [7] and for further reoptimisation of geometries, the PM3 method of the MOPAC 6.0 computer program was used [8,9]. GAUSSIAN 98 package program was finally used to perform *ab initio* calculations at HF/6-31G* level. Energy minimum molecular geometries were located by minimising energy, with respect to all geometrical coordinates without imposing any symmetry constraints.

The nature of the stationary points for compound **2** has been determined by virtue of the number of imaginary frequencies. For minimum state structures, only the real frequency value and in the transition state, only a single imaginary frequency value (with negative sign) was accepted [10].

The structure of the molecular transition state geometries were located by using the optimised geometries of the equilibrium molecular structure according to the procedure of Dewar *et al.* (keyword SADDLE) [11]. These geometry structures were then reoptimised by QST3 option at the HF/6-31G* level. The vibrational frequency of ground states and transition states were calculated by keyword FREQ.

Results and discussion

Corrected zero-point (ZPE^c) and total electronic (E_{el}) energies (where E₀ = E_{el} + ZPE^c) for the six configurational diastereoisomers of cycloundeca-1,2,4,5,7,8,10-heptaene (**2**), as calculated by HF/6-31G* level of theory are shown in Table 1. For single-point energy calculations both *ab initio* MP2/6-31G**/HF/6-31G* and DFT method (B3LYP/6-31G**/HF/6-31G*) were used. The axial symmetrical configuration constructed by a combination of two units of the same chirality and a unit of opposite chirality with a *cis* π bond (Z-RSR or Z-SRS) was found to be the most stable geometry of **2**, as calculated by HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* methods. Also, HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* calculations showed that the other configuration of this family, namely Z-RSS, with C₁ point group, is only 2.99, 4.20 and 5.32 kcal/mol above the Z-RSR diastereoisomer, respectively. The least stable configuration of the Z-isomer was constructed by a combination of three allenic moieties of the same chirality (Z-RRR, C₂), which is about 5.61, 7.17 and 6.55 kcal/mol above the Z-RSR isomer, as calculated by HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G*, respectively.

The most stable configuration of the E-isomer was the E-RRR configuration (with C₁ symmetry) which is 18.61, 14.99 and 17.20 kcal/mol less stable than the Z-RSR isomer, as calculated by HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* methods, respectively. Also, the other possible configurations of E-isomer, namely E-RSS and E-RSR are less stable than the E-RRR configuration by 5.31 and 10.64 kcal/mol using HF/6-31G**/HF/6-31G*, 1.92 and 8.92 using MP2/6-31G**/HF/6-31G*, 0.31 and 6.23 kcal/mol according to B3LYP/6-31G**/HF/6-31G* methods, respectively.

In the E-family, the E-RRR configuration (with C₁ point group) is flexible and can be converted to the C₁' structure via an axial symmetrical transition state with C₂ symmetry. The

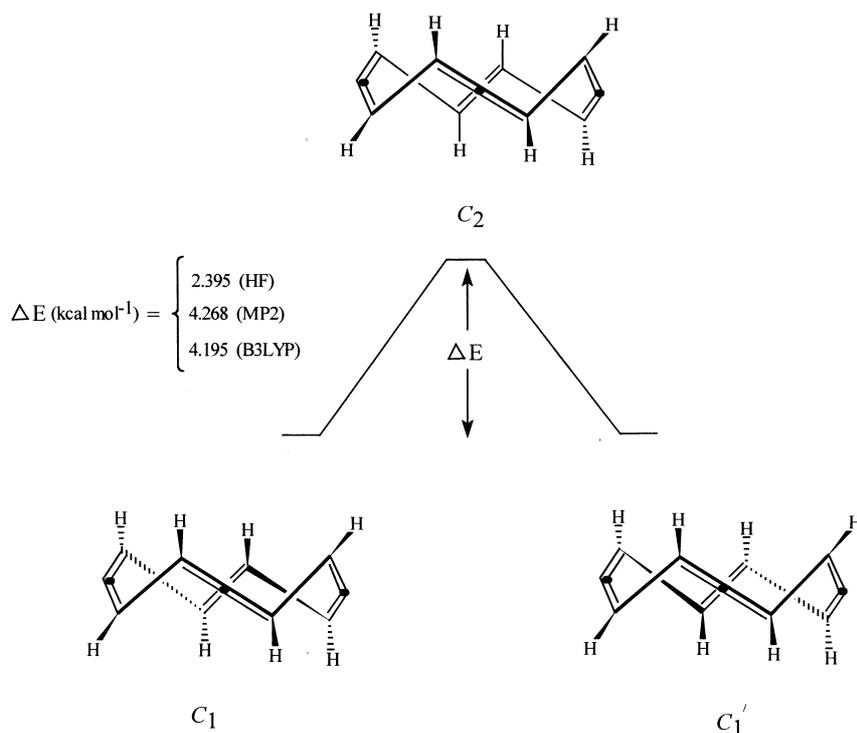


Fig.1 Calculated HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* profile for conformational interconversion of E-RRR configuration, with C_2 symmetry.

energy barrier of this conformational interconversion is about 2.39, 4.27 and 4.20 kcal/mol, as calculated by HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* methods, respectively.

The carbon-carbon bond lengths for various configurational diastereoisomer of **2**, as calculated by the HF/6-31G* level, are given in Table 1. Computed bond lengths of the $C(sp^2)$ - $C(sp)$ double bonds and $C(sp^2)$ - $C(sp^2)$ single bonds fell in comparatively restricted regions: 1.296-1.305 and 1.475-1.505 Å, respectively (see Table 1). Internal angles and torsional parameters for configurational diastereoisomers of **2** are shown in Fig. 1. The $C=C=C$ fragments are bent in various configurations of **2** and are slightly contracted from the normal value of 180° (see Fig. 1).

The $C(sp^2)$ - $C(sp^2)$ - $C(sp^2)$ - $C(sp^2)$ arrangements in the allenic moieties of the twist and crown configurations are fairly twisted (1.6 - 33.8°) from their minimum energy states (with a corresponding angle of 90°) as a result of ring strain.

In conclusion, HF, MP2 and B3LYP calculations provided useful information concerning both energetical and structural properties of the possible configurations of **2**. HF/6-31G**/HF/6-31G*, MP2/6-31G**/HF/6-31G* and B3LYP/6-31G**/HF/6-31G* calculations showed that the most stable *Z*-isomer is 18.61, 14.99 and 17.20 kcal mol⁻¹ respectively, more stable than the most stable *E*-isomer. This fact could be explained by greater torsional strain in the most stable configuration of *E*-family (*E*-RRR, C_1), in which the dihedral angles (formed by $C(sp^2)$ - $C(sp^2)$ - $C(sp^2)$ - $C(sp^2)$ arrangements) in the allenic units are twisted from their minimum energy state (with a corresponding angle of 90°) by 20° , 7.3° and 29.3° , while in the most stable configuration of *Z*-family (*Z*-RSR, C_2), these dihedral angles are twisted from their minimum energy state by only 8.1° , 20.9° and 8.1° .

The authors acknowledge helpful discussions with Dr F. Deyhimi and material support from Arak Branch, Islamic Azad University.

Received 13 October 2001; accepted 9 June 2002
Paper 01/1103

References

- 1 V.I. Minkin, M.N. Glukhovtsev and B. Ya. Simkin, *Aromaticity and Antiaromaticity, Electronic and Structural Aspects*, Wiley-Interscience, New York, (1994).
- 2 P.J. Garratt, *Aromaticity*, Wiley-Interscience, New York (1986).
- 3 A. Greenberg and J.F. Liebman, *Strained Organic Molecules*, Academic Press, New York, (1978); K.B. Wiberg, *Angew. Chem. Int. Ed. Engl.*, **25**, 312 (1986).
- 4 R.P. Johnson, *Chem. Rev.*, **89**, 1111 (1989).
- 5 P.G. Garratt, K.C. Nicolaou and F. Sondheimer, *J. Am. Chem. Soc.*, **95**, 4582 (1973).
- 6 M.J. Frisch, G.W. Trucks, 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. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malik, A.D. Rabuck, K. Raghavachar, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanyakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople. GAUSSIAN 98 (Revision A.3) Gaussian Inc. Pittsburgh, PA, USA (1998).
- 7 Serena Software, Box 3076, Bloomington, IN, USA
- 8 J.J.P. Stewart, *J. Comput. Chem.*, **10**, 221(1989)
- 9 J.J.P. Stewart, *QCPE 581*, Department of Chemistry, Indiana University, Bloomington, IN., USA.
- 10 J.W. McIver, Jr., *Acc. Chem. Res.*, **7**, 72 (1974); O. Ermer, *Tetrahedron*, **31**, 1849 (1975).
- 11 M.J.S. Deware, E.F. Heally and J.J.P. Stewart, *J. Chem. Soc., Faraday Trans.*, **80**, 227 (1984).