Dynamics of Cyclic Allenes. Conformational Energy Surface of Cyclodeca-1,2,4,5-tetraene†

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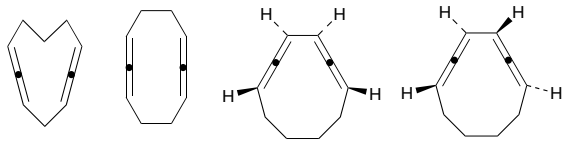
Iterative molecular mechanics calculations using Boyd's computer program MOLBUILD and AM1 semi-empirical SCF MO calculations for two diastereoisomeric forms of cyclodeca-1,2,4,5-tetraene are reported for four conformations and three transition states for conformational interconversions.

Allenes are an important class of unsaturated hydrocarbons which contain two double bonds in an orthogonal geometry.[1,2] Ring constraints bend and twist the normally linear perpendicular allene and engender substantial strain and resultant kinetic reactivity.[3]

Monocyclic medium-ring diallenes with the allene groups in a ring that has more than nine members appear to be fairly stable. Simple monocyclic diallenes possess two chiral centres and should exist in two diastereoisomeric forms, one diastereoisomer being racemic and the other a *meso* compound. Such isomers have been isolated in the case of the 12-membered diallene cyclododeca-3,4,9,10-tetraene-1,7-dione[4] and 14-membered diallene cyclotetradeca-3,4,10,11-tetraene-1,8-dione.[4] The cyclic diallenes cyclodeca-1,2,5,6-tetraene (**1**)[5] and cyclodeca-1,2,6,7-tetraene (**2**)[6] are available *via* the bis(dibromocarbene) adducts of cycloocta-1,4-diene and cycloocta-1,5-diene, respectively. However, treatment of the bis(dibromocarbene) adduct of cycloocta-1,3-diene with methyllithium at −30 °C produces cyclodeca-1,2,4,5-tetraene as an elusive compound that affords a good yield of bicyclo[6.2.0]deca-1,7,9-triene.[7]



1 **2** **3** **4**

While the conformational properties of **1** and **2** have been studied both experimentally[8] and theoretically,[9] there are no published experimental or theoretical data on the structure or conformational features of *meso*- and (±)-cyclodeca-1,2,4,5-tetraene (**3** and **4**). In view of the success of iterative molecular mechanics calculations and AM1 semi-empirical SCF MO calculations in investigating the conformational properties of cyclic allenes[8–11] and diallenes,[8,12,13] we carried out corresponding investigations of **3** and **4** and report here our results.

Experimental

MM calculations were carried out on an IBM 3390 computer, using Boyd's iterative computer program MOLBUILD.[14,15] The parameters used in these calculations have been previously reported.[16,17] The conjugation energy terms for **3** and **4** were obtained from the torsional angle of single bonds flanked by two double bonds. A two-fold potential with a stabilization (negative strain energy) of 4.24 kcal mol^{-1} for the planar (0 and 180°) arrangement was chosen because this reproduces experimentally the barrier to rotation seen in buta-1,3-diene.[18]

Semi-empirical calculations were carried out using the AM1 method with the MOPAC 6.0 program,[19] implemented on a VAX 4000-300 computer. Energy-minimum geometries were located by minimizing 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 conformations and the procedure of Dewar *et al.*[20] (keyword SADDLE). We have checked that all of the conformations obtained in the present work are true local-energy minima and energy maxima, as evidenced by the fact that they all are calculated to have $3N-6$ and $3N-7$ real vibrational frequencies, respectively.[21]

Results and Discussion

meso-*Cyclodeca*-1,2,4,5-*tetraene* (**3**).—The results of MM calculations for important geometries of **3** are shown in Table 1. The unsymmetrical twist (**3-T**) conformation is calculated to have the lowest strain energy. By constraining the torsional angle ϕ_{89101} from 74 to 12°, a smooth conformational change occurred, leading to a transition state (**3T→3TC**)$^{\#}$. Further changing of the same torsional angle yielded another energy minimum, namely the twist-chair (**3-TC**) conformation, which lacks symmetry. Since **3-TC** is calculated to be 0.8 kcal mol^{-1} above **3-T**, it is expected to be significantly populated at room temperature. The calculated strain-energy barrier for interconversion of **3-T** and **3-TC** is 4.6 kcal mol^{-1}. The plane-symmetrical chair (**3-C**) geometry is a transition state between the chiral **3-TC** and its mirror-image conformation **3-TC′**. The calculated strain energy for **3-C** is *ca*. 4.9 kcal mol^{-1}. This pathway has the lowest calculated energy of the several pathways investigated.

The relevant structural parameters and heats of formation ($\Delta H_f°$) for various geometries of **3**, as calculated by the AM1 method, are given in Table 1 and Fig. 1. The twist (**3-T**) conformation has the lowest calculated heat of formation. The calculated heat of formation for **3-TC** is *ca*. 1.8 kcal mol^{-1} above that of **3-T**. The structure of the transition-state geometries (**3T→3TC**)$^{\#}$ and **3-C** were obtained from MOPAC 6.0 using the optimized geometries of **3-T**, **3-TC** and **3-TC′** conformations and the procedure of Dewar *et al.* (Keyword SADDLE).[20] The agreement between the AM1 and MM results is fairly good (Table 1).

Representative structural parameters for the important geometries of the *meso*-isomer (**3**) are given in Table 1. The internal angles are close to the unstrained values in **3-T** and **3-TC**, but fairly expanded in transition-state geometries. The

Table 1 Calculated structural parameters [bond angles (θ) and dihedral angles (ϕ) in °] and energies (kcal mol^{-1}) in various forms of *meso*-cyclodeca-1,2,4,5-tetraene (**3**)

	3-T, C_1		**3-TC**, C_1		(**3-T→3-TC**)$^{\#}$, C_1		**3-C**, C_s	
	MM	AM1	MM	AM1	MM	AM1	MM	AM1
E_s[a]	6.08		6.92		10.68		10.96	
ΔE_s[b]	0.00		0.84		4.60		4.88	
ΔH_f[c]		75.27		77.09		79.85		82.08
$\Delta\Delta H_f$[b]		0.00		1.82		4.58		6.81
θ_{123}	170	169	166	168	167	168	165	166
θ_{234}	121	120	120	119	119	118	118	118
θ_{345}	120	120	120	119	119	119	118	118
θ_{456}	167	171	165	168	165	170	165	167
θ_{567}	123	123	122	122	122	122	122	122
θ_{678}	111	110	110	109	112	110	113	112
θ_{789}	113	113	116	115	114	114	120	120
θ_{8910}	114	113	116	117	118	119	120	120
θ_{9101}	112	112	114	113	116	116	113	112
θ_{1012}	123	123	121	121	123	122	122	122
ϕ_{10134}	−76	−76	−70	−71	−84	−77	−72	−71
ϕ_{2345}	0	0	−8	−10	−9	−10	0	0
ϕ_{3467}	77	73	66	66	74	71	72	70
ϕ_{5678}	−91	−87	−111	−106	−106	−98	−129	−128
ϕ_{6789}	82	85	119	121	110	115	82	84
ϕ_{78910}	−120	−132	−58	−68	−95	−95	0	0
ϕ_{89101}	74	73	−43	−35	12	−1	−81	−83
ϕ_{91012}	48	48	125	121	98	102	129	128

[a]Strain energy. [b]Relative to the best conformation of the same compound. [c]Heat of formation.

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Table 2 Calculated strain energies in different conformations of *meso*-cyclodeca-1,2,4,5-tetraene (**3**) and (±)-cyclodeca-1,2,4,5-tetraene (**4**

	Strain-energy contributions (kcal mol^{-1})						
	3-T, C_1	**3-TC**, C_1	(**3-T**→**3-TC**)$^{\#}$, C_1	**3-C**, C_s	**4-TBC**, C_s	**4-TCC**, C_2	**4-T**, C_2
Bond stretching	0.25	0.27	0.39	0.42	0.24	0.26	0.41
Bond-angle bending	2.74	4.91	5.57	8.02	1.90	4.78	11.14
Torsional strain	2.02	0.25	2.68	0.47	2.92	1.03	0.82
Out-of-plane bending	0.21	0.58	0.16	0.36	0.46	0.37	0.54
Non-bonded interactions	0.86	0.91	1.88	1.69	0.76	0.24	1.54
Total strain energy	6.08	6.92	10.68	10.96	6.28	6.68	14.45

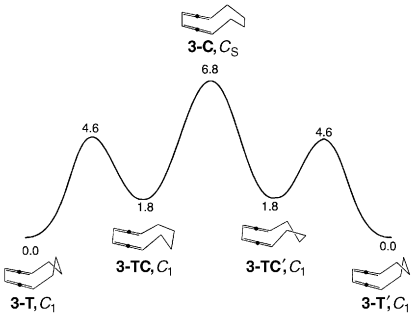

Fig. 1 Calculated AM1 profile for conformational enantiomerization of **3-T** and **3-T′** *via* the plane-symmetrical chair (**3-C**) geometry

Table 3 Calculated structural parameters [bond angles (θ) and dihedral angles (ϕ) in °] and energies (kcal mol^{-1}) in various forms of (±)-cyclodeca-1,2,4,5-tetraene (**4**)

	4-TBC, C_2		**4-TCC**, C_2		**4-T**, C_2	
	MM	AM1	MM	AM1	MM	AM1
E_s[a]	6.28		6.68		14.45	
ΔE_s[b]	0.00		0.40		8.17	
ΔH_f[c]		75.45		77.13		87.75
$\Delta\Delta H_f$[b]		0.00		1.68		12.30
θ_{345}	120	119	118	117	119	116
θ_{456}	172	172	167	168	163	164
θ_{567}	124	124	123	123	119	120
θ_{678}	113	112	112	112	116	116
θ_{789}	112	113	116	116	121	123
ϕ_{2345}	−62	−54	−33	−34	−25	−27
ϕ_{3467}	72	77	73	76	68	75
ϕ_{5678}	−31	−45	−123	−119	−130	−129
ϕ_{6789}	−65	−58	95	97	39	34
ϕ_{78910}	161	155	−69	−77	−26	−26

[a]Strain energy. [b]Relative to the best conformation of the same compound. [c]Heat of formation.

C═C═C moieties are bent in various geometries of **3** and they are 10–15° compressed from the normal value of 180°. The C(sp^3)-C(sp^2)-C(sp^2)-C(sp^2) arrangements (ϕ_{3467} and ϕ_{10134}) in the allenic moieties of all forms are fairly twisted from their energy minima at 90°, as a result of ring strain.

Contributions to the overall strain energy in the four geometries of the *meso*-diallene **3**, as calculated by the MM procedure, are shown in Table 2. The bond and out-of-plane bending terms are small in all forms. The transition-state geometries have higher bond-angle and torsional terms than the minimum-energy conformations. The other strain-energy contributions are substantial and vary over a relatively wide range of values.

(±)-*Cyclodeca*-1,2,4,5-*tetraene* (**4**).—Three geometries (two energy minima and a transition state) were found to be necessary in a description of the conformational properties of the (±)-diallene (**4**). The most stable conformation of **4**, as calculated by the MM method, is the axial symmetrical twist-boat-chair (**4-TBC**) (Fig. 2). The calculated torsional and internal angles of **4-TBC** are given in Table 3. The calculated strain energy for the second energy-minimum conformation, *viz*. twist-chair-chair (**4-TCC**) (C_2) is 0.4 kcal mol^{-1}. Conformations **4-TBC** and **4-TCC** are important because they are expected to be significantly populated at room temperature. The calculated strain-energy barrier (8.17 kcal mol^{-1}) for interconversion of the two forms is substantial. This feature makes a dynamic NMR spectroscopic study of the (±)-isomer **4** attractive.

The relevant structural parameters and heats of formation (ΔH_f°) for various geometries of **4** are given in Table 3. The

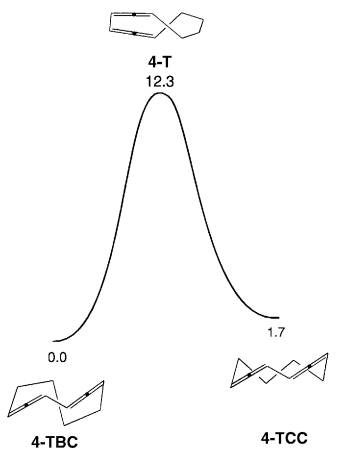

Fig. 2 Calculated AM1 profile for conformational interconversion of **4-TBC** and **4-TC** *via* the axial-symmetrical **4-T** geometry

twist-boat-chair (**4-TBC**) conformation has the lowest calculated heat of formation. The calculated heat of formation of **4-TCC** is 1.68 kcal mol^{-1} above that of **4-TBC**. The structure of the transition state (**4-T**) was obtained from MOPAC 6.0 using the optimized geometries of **4-TBC** and **4-TCC** conformations and the procedure of Dewar *et al.*[20] (see Fig. 2).

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