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Configurational Properties of Cyclonona-1,2,4,5,7,8-hexaene and Cyclododeca-1,2,5,6,9,10-hexaene†

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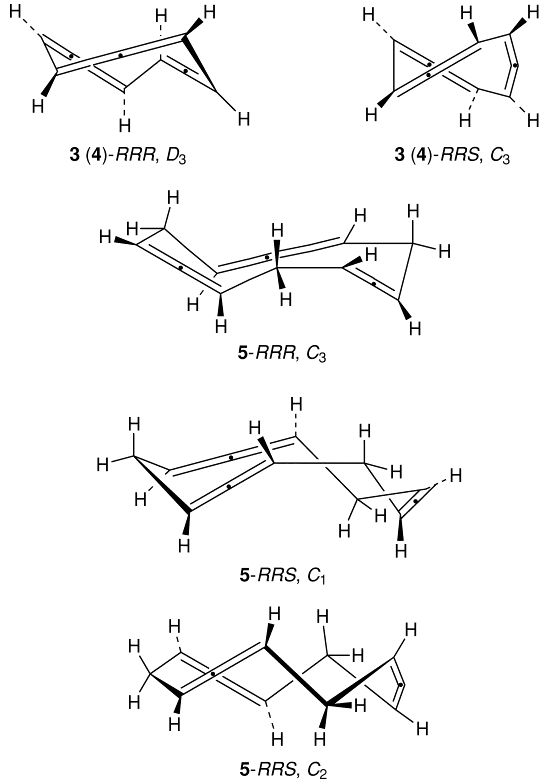
AM1 semi-empirical SCF MO calculations for the structure optimization and configurational properties of cyclonona-1,2,4,5,7,8-hexaene **3**, its hexamethyl derivative **4** and cyclododeca-1,2,5,6,9,10-hexaene **5** show that the combination of three allenic units of the same chirality yields an enantiomeric pair which is the most stable configuration of **3**, **4** and **5**.

Benzene **1** and *Z*,*Z*,*Z*-cyclonona-1,4,7-triene (trishomobenzene) **2**[1] can undergo a distinct expansion process, which involves insertion of a sp-hybridized carbon atom into each carbon–carbon double bond to produce cyclonona-1,2,4,5,7,8-hexaene **3** and cyclododeca-1,2,5,6,9,10-hexaene **5**, respectively. The protons in these expanded structures are in similar environments to those in the parent molecules. Since compounds **3** and **5** differ from **1** and **2** by the number of carbon atoms (and thus by size), these expanded structures are expected to manifest special configurational features. Compounds **3** and **5**, with three allenic moieties, could experience six-electron cyclic interactions of both the in-plane and out-of-plane π bonds of the three allenic chromophores.[2–4] This structural feature suggests that combination of three units of the same chirality yields an enantiomeric pair (*RRR* or *SSS*), while combination of two units of the same chirality and a unit of opposite chirality produces another enantiomeric pair (*RRS* or *SSR*) (see Scheme 1).


3 (**4**)-*RRR*, D_3

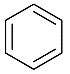
3 (**4**)-*RRS*, C_3

5-*RRR*, C_3

5-*RRS*, C_1

5-*RRS*, C_2

Scheme 1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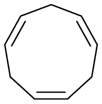
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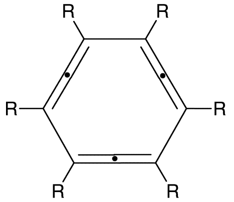
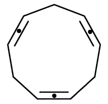


3 R = H
4 R = CH_3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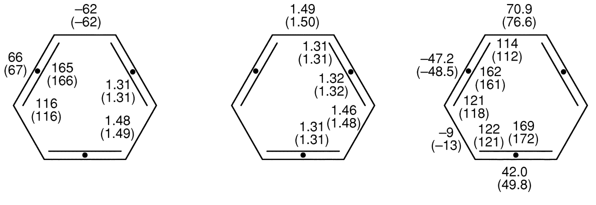
Intrigued by the fascinating molecular structures of cyclic triallenes **3** and **5**, we carried out semi-empirical AM1 SCF MO calculations[5] on six possible configurations of **3**–**5**. Even though compounds **3**–**5** have not been synthesized, it is possible to learn something about them by using theoretical methods that have proved to be reliable in other applications.[6]

Calculations

Initial estimates of the geometry of structures **3**–**5** were obtained by a molecular-mechanics program PCMODEL (88.0)[7] followed by full minimization using semi-empirical AM1[8] method in the MOPAC 6.0 computer program,[5,9] implemented on a VAX 4000-300 computer. Optimal geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structure of the transition-state geometries was obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*[10] (keyword SADDLE). All geometries were



RRR, D_3 *RRS*, C_2 *RRS*, C_2

Fig. 1 Calculated structural parameters (bond lengths in Å, bond angles and dihedral angles in degrees) in *RRR* and *RRS* configurations of **3**: the parameters shown in parentheses belong to the hexamethyl derivative **4**

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Table 1 Calculated energies (kJ mol^{-1}) in *RRR* and *RRS* configurations of cyclonona-1,2,4,5,7,8-hexaene **3**, 1,3,4,6,8,9-hexamethylcyclonona-1,2,4,5,7,8-hexaene **4** and cyclododeca-1,2,5,6,9,10-hexaene **5**

	3		**4**		**5**		
Energy	*RRR*, D_3	*RRS*, C_2	*RRR*, D_3	*RRS*, C_2	*RRR*, C_3	*RRR*, C_1	*RRS*, C_2
ΔH^{o}_{f}	678.9	735.7	498.7	561.8	516.6	517.6	529.3
$\Delta\Delta H^{o}_{f}{}^{a}$	0.0	56.8	0.0	63.1	0.0	1.0	11.7^{b}

[a] Relative to the best configuration of the same compound. [b] Relative to the *RRS*, C_1 conformation.

characterized as stationary points, and true local energy-minima and transition states on the potential energy surface were found using keyword FORCE. All energy-minima and transition-state geometries obtained in this work are calculated to have $3N$-6 and $3N$-7 real vibrational frequencies, respectively.[11]

Results and discussion

Heats of formation (ΔH^{o}_{f}) for the six diastereoisomers of cyclic triallene **3**, its hexamethyl derivative **4** and the skipped cyclic triallene **5**, as calculated by AM1 method, are shown in Table 1. The highly symmetrical configurations of **3**–**5**, constructed by a combination of three allenic units of the same chirality (*RRR* or *SSS*), are calculated to be the most stable geometries. The other configurations of **3** and **4** which have a two-fold axis of symmetry, are 57 and 63 kJ mol^{-1} less stable than the ground state geometry. The most stable conformation of the skipped cyclic triallene **5**, with *RRS* (or *SSR*) configuration, lacks symmetry and is only 1 kJ mol^{-1} above the symmetrical C_3 configuration. The axial symmetrical geometry of the *RRS* isomer is calculated to be a transition state for conformational isomerization of the unsymmetrical conformation, see Table 1.

Important structural parameters for the configurational diastereoisomers of **3** and **4** are shown in Fig. 1. The C=C=C moieties are bent in both configurations of **3** and **4** and they are 8–19° compressed from the normal value of 180°. The C=C–C bond angles in all geometries of the hexamethyl derivative **4** are 1–3° more compressed in comparison to those in **3**, as a result of the methyl substituents.

The C_{sp^2}–C_{sp^2}–C_{sp^2}–C_{sp^2} arrangements in the allenic moieties of the *RRR* and *RRS* configurations of **3** and **4** are fairly twisted (23–48°) from their energy minimum at 90°, as a result of ring strain. However, the extent of this torsional deformation in the *RRR* (D_3) diastereoisomer is much smaller.

The carbon–carbon bond lengths for configurational diastereoisomers of the skipped cyclic triallene **5** are given in Fig. 2. In compound **5**, a saturated carbon atom separates two allenic chromophores, thus allowing at most homoconjugation[12] between the π-bonds. Computed bond lengths of the C_{sp^2}–C_{sp} double bonds and C_{sp^2}–C_{sp^3} single bonds fell in comparatively restricted regions: 1.301–1.303 and 1.480–1.491 Å, respectively.

Internal angles and torsional parameters for configurational diastereoisomers of **5** are shown in Fig. 2. The C=C=C fragments are bent in various configurations of **5** and they are slightly contracted from the normal value of 180°. The largest internal angle deformations are displayed by the axial symmetrical *RRS* configuration. Some of the C–C–C bond angles are expanded by about 10° from their normal values (see Fig. 2).

In conclusion, AM1 calculations provide a fairly clear picture of the configurations of cyclononahexaene **3**, its hexamethyl derivative **4** and the skipped cyclic triallene **5** from both structural and energetic points of view. According to these calculations, the combination of three allenic units of the same chirality yields an enantiomeric pair, which is the most stable configuration of **3**, **4** and **5**. It would be valuable, of course, to have direct structural data on **3**–**5** for comparison with the results of the AM1 semi-empirical SCF MO calculations.

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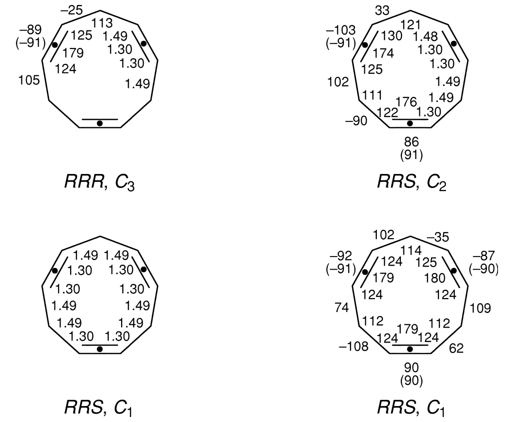

RRR, C_3 *RRS*, C_2

RRS, C_1 *RRS*, C_1

Fig. 2 Calculated structural parameters (bond lengths in Å, bond angles and dihedral angles in °) in *RRR* and *RRS* configurations of **5**. The torsional angles shown in parentheses belong to the allenic H–C_{sp^2}–C_{sp^2}–H arrangements

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