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Ab initio study of configurational and conformational properties of cyclodeca-1,2,4,6,7,9-hexaene and cyclodeca-1,2,4,6,8,9-hexaene†

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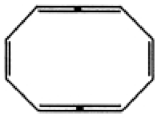
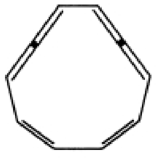
Ab initio molecular orbital and density functional theory (DFT) calculations, used to calculate the structure optimisation and configurational features of cyclodeca-1,2,4,6,7,9-hexaene (**1**) and cyclodeca-1,2,4,6,8,9-hexaene (**2**), showed that the important structures in compound **1** are: *RZRZ* (D_2 symmetry), *RZSZ* (C_{2h} symmetry) and for compound **2** are: *RSZZ* (C_1 symmetry), *RRZZ* (C_2 symmetry).

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 centers and should exist in two diastereoisomeric forms, one diastereoisomer being racemic and the other a *meso* compound. Cyclodeca-1,2,4,6,7,9-hexaene (**1**) and cyclodeca-1,2,4,6,8,9-hexaene (**2**), with two allenic moieties, could experience eight-electron cyclic interactions of the out-of-plane π-bonds and four-electron interactions of the in-plane π-bonds[4-7].

Conceptually, **1** and **2** may be regarded to be constructed by inserting a carbon atom in two of the carbon-carbon double bonds of cycloocta-1,3,5,7-tetraene. In compound **1**, structural features suggest that the combination of two allenic units of the same chirality yields an enantiomeric pair (*RR* and *SS*) of D_2 symmetry for *ZZ* or *EE*-isomers (*RZRZ*, D_2, *RERE*, D_2) and the combination of two allenic units of the opposite unit chirality yields for following isomers: *RZSZ*, C_{2h}, *RZSE*, C_1, *RESE* (⊥), C_2 and *RESE* (‖), C_1. The ⊥ and ‖ symbols are used to indicate that the two double bonds are crossed and parallel, respectively, see Scheme 1.

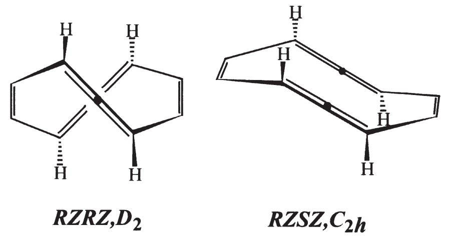


(1)

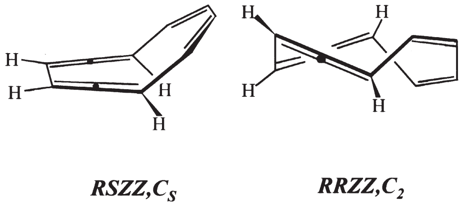


(2)

In compound **2**, the combination of the two allenic units of the same chirality yields an enantiomeric pair (*RR* and *SS*) of C_2 symmetry for the *Z*- or *E*-isomer (*RRZZ*, C_2, and *RREE*, C_2). The combination of the two units of opposite chirality and two π-bonds yields the following isomers: *RSZZ*, C_1; *RSZE*, C_1; *RSEE*, C_1; in which the RSZZ configuration (with the C_1 point group) is flexible and can be converted to a C'_1 structure *via* a plane symmetrical transition state structure (see Scheme 2). Intrigued by the fascinating molecular structural aspects of cyclic diallenes **1** and **2**, we carried out *ab initio* and density functional theory (DFT) calculations[8-10] to investigate the possible configurations of **1** and **2**.



Scheme 1



Scheme 2

In compound **1**, the combination of two allenic units of opposite chirality with two cis π bond yields a *meso-form* (*RZSZ*) of C_{2h} symmetry, which is the most stable configuration of **1**. The combination of two allenic moieties of the same chirality with two *cis*-olefinic π-bond yields an enantiomeric pair (*RZRZ* or *SZSZ*) of D_2 symmetry which was found to be about 0.33 kJ mol^{-1} less stable than the *RZSZ* isomer, as calculated by the HF/6-31G* method. B3LYP/6-31G*//HF/6-31G* calculations show that the *RZRZ* (or *SZSZ*) configuration with D_2 symmetry is the most stable configuration of **1**. *RZSZ* and *RZRZ* configurations are particularly important because they are expected to be significantly populated at room temperature. The calculated HF/6-31G* results show also that by conversion of one of the two *cis*-π-bonds in the *RZSZ* isomer, to a *trans*-π-bond, the energy of the *RZSE* isomer rises by about 34 kcal mol^{-1} above the *RZSZ* isomer. As a result, the *RZSE* configuration is not expected to be populated at room temperature. In compound **2**, HF/6-31G* calculations predict that the combination of two allenic chromophores of the same chirality yields an enantiomeric pair of axial symmetrical configuration (*RRZZ*, C_2), which is also the most stable diastereoisomer of **2**. Both MP2/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* calculations show that the *meso*-(*RSZZ*, C_1) and *dl*-(*RRZZ*) compounds are particularly important because they are expected to be significantly populated at room temperature. HF/6-31G* studies show that compound **2** is less stable than compound **1** by about 10.50 kcal mol^{-1}. This fact could be explained by the greater torsional strengths in compound **2**, in which the dihedral angle (formed by the C_{sp2}–C_{sp2}–C_{sp2}–C_{sp2}

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arrangement) in the allenic unit is twisted from its minimum energy state (with a corresponding angle of 90°) by 13.7°, while in the most stable configuration of compund **1** (*RZSZ*) with C_{2h} symmetry, this dihedral angle is twisted from its minimum energy state by only 7.3°.

Ab initio methods: HF/6-31*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, B3LYP/6-31G*//HF/6-31G*

References: 16

Schemes: 2

Figures: 6

Tables: 2

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