Conformational Properties of Cyclododeca-1,5,9-triyne†

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Semi-empirical AM1 SCF-MO calculations are used to calculate the structure optimization and conformational interconversion pathways in cyclododeca-1,5,9-triyne; two symmetrical energy-minimum conformations, *viz*. chair (D_3) and twist-boat (C_2), with similar strain energies are found which are separated by a fairly low (9.6 kJ mol^{-1}) energy barrier.

Cyclododeca-1,5,9-triyne (**1**), with three acetylenic chromophores alternatively inserted in carbon–carbon bonds of cyclohexane, could experience six-electron cyclic interactions of both the in-plane and out-of-plane π bonds of the three acetylene moieties, and might exhibit homoaromaticity.[1] This 'exploded cyclohexane' 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 conformations of cyclohexane, will be greatly reduced.[2–4] *Ab initio* calculations with the STO-3G minimal basis set have been reported[1] for the chair-like (D_3) and planar D_{3h} geometries of **1**. According to these calculations the D_3 conformation is 67 kJ mol^{-1} more stable than D_{3h}. The photoelectron spectrum of **1** has been interpreted in terms of a chair-like conformation of D_3 symmetry.[1]

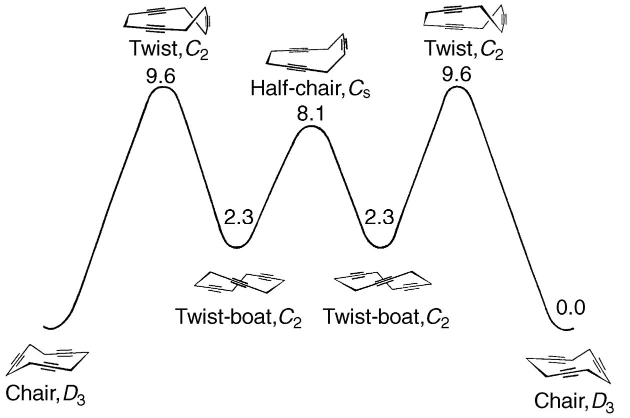

Fig. 1 Calculated strain energy (kJ mol^{-1}) profile for the degenerate interconversion of the chair conformation of cyclododeca-1,5,9-triyne with its mirror image geometry *via* twist-boat intermediates

We present the results of Austin Model 1 (AM1) semi-empirical SCF-MO calculations[5] on **1** that allow interesting conclusions to be drawn about the conformational properties of this molecule. Two symmetrical energy-minimum conformations, *viz*. chair (D_3) and twist-boat (C_2), with similar strain energies[6] are found which are separated by a fairly low energy barrier. The planar D_{3h} geometry of **1** was found to be about 26.9 kJ mol^{-1} less stable than the D_3 conformation.

Semi-empirical calculations were carried out using the AM1 method with the MOPAC 6.0 program[7,8] 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 structures according to the procedure of Dewar *et al.*[9] (using keyword SADDLE). All structures were characterized as stationary points, and true local energy-minima and energy-maxima on the potential energy surface were found using the keyword FORCE. All energy-minima and energy-maxima geometries obtained in this work are calculated to have $3N-6$ and $3N-7$ real vibrational frequencies, respectively.[10]

Results and Discussion

The results of semi-empirical AM1 calculations for various molecular geometries of cyclododeca-1,5,9-triyne (**1**) are shown in Table 1 and Fig. 1. The conformational possibilities available to **1** parallel those of cyclohexane.[11] Thus, chair and twist-boat conformations should be accessible. The chair conformation, which has D_3 symmetry, is calculated to have the lowest heat of formation (ΔH_f°). Since the twist-boat form has a higher (by *ca*. 2.3 kJ mol^{-1}) ΔH_f than the chair form, it is expected to be significantly populated at room temperature. The chair conformation is the same as the structure determined by photoelectron spectroscopy.[1]

The energy surface for the interconversion of the energy-minimum conformations of **1** was investigated in detail by changing different torsional angles. The results are shown in Fig. 1. There are two distinct, different transition states (not counting mirror images) which are required to describe the conformational dynamics in cyclododeca-1,5,9-triyne. The internal and torsional angles of these transition states are given in Table 1.

The simplest conformational process, and the one with the lowest barrier, is the degenerate interconversion of the chair conformation with its mirror image *via* the twist-boat intermediate. If this process is fast the time-averaged symmetry of the chair conformation becomes D_{3h}, which is the maximum symmetry allowed by the chemical structure of cyclododeca-1,5,9-triyne. A second, and higher-energy, process undergone by the chair conformation is also degenerate, and involves the planar transition state, which has D_{3h} symmetry. The calculated heat of formation for planar D_{3h} geometry is 26.9 kJ mol^{-1}, which is much higher than those for twist and half-chair geometries (see Table 1).

Two significant differences can be anticipated between the conformational features of cyclododeca-1,5,9-triyne (**1**) and cyclohexane. The first derives from the fact that torsional effects and transannular van der Waals repulsion should diminish in **1**, since the dimensions of the ring will be magnified while the CH_2CH_2 groups will remain unchanged in size. Consequently, conformations such as chair and twist-boat should hardly differ in energy from one another. By comparison, cyclohexane exists mainly in the chair conformation ($>99\%$) at room temperature.[11]

The other conformational feature of **1** concerns its flexibility. The ease with which the $C{-}C{\equiv}C$ bond angles can be deformed from linearity and the large number of sp carbon atoms over which angle strain can be spread will practically reduce the barriers to conformational interconversions in **1**.

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Table 1 Heats of formation, bond angles and dihedral angles for cyclododeca-1,5,9-triyne

Feature	Chair D_3	Twist-boat C_2	Twist C_2	Half-chair C_S	Planar D_{3h}
ΔH_f°/kJ mol^{-1}	494.5	496.8	504.1	502.6	521.4
$\Delta\Delta H_f^\circ$/kJ mol^{-1}	0.0	2.3	9.6	8.1	26.9
Bond angle (θ/°)					
θ_{123}	178	177	176	177	176
θ_{234}	112	112	112	112	116
θ_{345}	112	113	113	113	116
θ_{456}	178	177	178	178	176
θ_{567}	178	178	176	178	176
θ_{678}	112	113	116	115	116
θ_{789}	112	113	116	115	116
$\theta_{8,9,10}$	178	178	176	178	176
$\theta_{9,10,11}$	178	177	178	178	176
$\theta_{10,11,12}$	112	113	113	113	116
$\theta_{11,12,1}$	112	112	112	112	116
$\theta_{12,1,2}$	178	177	176	177	176
Dihedral angle (ϕ/°)					
ϕ_{2345}	51	46	49	50	0
ϕ_{3478}	-69	11	-27	-51	0
ϕ_{6789}	51	-51	0	0	0
$\phi_{7,8,11,12}$	-69	11	-27	51	0
$\phi_{10,11,12,1}$	51	46	49	-50	0
$\phi_{11,12,3,4}$	-69	-83	-76	0	0

[a] The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation (ΔH_f°) for that geometry and the most stable conformation of the molecule.[6]

Thus, the barrier separating the chair from the twist-boat conformation should be only a small fraction of the 45 kJ mol^{-1} required for the same conformational change in cyclohexane.[11]

In conclusion, AM1 calculations provide a picture of the conformations of cyclododeca-1,5,9-triyne (**1**) from both the structural and energetic points of view. Compound **1** is predicted to exist as a mixture of chair (D_3) and twist-boat (C_2) conformations. There is good agreement between the AM1 structure of the chair form and the photoelectron results.[1]

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