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Effect of electronic interactions between double bonds on the conformational flexibility of 1,4-cyclohexadiene

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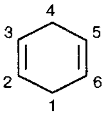
The electronic structure of 1,4-cyclohexadiene for various angles between the double bond planes has been calculated by the AM1 method. The effects of through-bond and through-space interactions, which result in flattening and unflattening, respectively, are oppositely directed. These effects are specified for various bending angles. In addition to steric factors, electronic factors affect the conformational flexibility of 1,4-cyclohexadiene .

Key words: conformational analysis; 1,4-cyclohexadiene, conformational flexibility.



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It has been found previously by experimental[1–3] and theoretical[4,5] methods that the 1,4-cyclohexadiene molecule (**1**) can undergo extraplanar oscillations with large amplitudes (±30°), characterized by variations of the angle between the planes of the double bonds.

This high conformational flexibility has been explained[4,5] by the effect of oppositely directed steric factors: angle strain of the saturated C atoms, which is maximum in the flat conformation, on the one hand, and 1,2-allylic strain, which flattens the molecule, on the other hand.

However, it is known that the double bonds in 1,4-cyclohexadiene are not isolated:[6,7] they are able to interact either by direct overlap of p_z-orbitals of the olefin C atoms through space or by overlap of these orbitals with the pseudo-π-orbitals of the methylene groups. These effects correspond to through-space interaction (TSI) and to through-bond interaction (TBI), respectively. The strength of TSI depends mainly on the distance between the interacting groups, but the degree of TBI is determined primarily by the availability of conditions for the overlapping of orbitals, that is, by the type of molecular conformation.[6,8]

Through-bond interaction in 1,4-cyclohexadiene stabilizes the flat conformation, which is the most favorable for the overlapping of the corresponding orbitals, while through-space interaction stabilizes the boat conformation with closely situated π-systems of double bonds. The type of the equilibrium conformation and the conformational flexibility of a cycle should depend on the relationship between these electronic effects. The predominance of TSI or TBI is determined by the order of orbitals $\pi^{+}_{C=C}$ and $\pi^{-}_{C=C}$. If the $\pi^{+}_{C=C}$ orbital has higher energy than $\pi^{-}_{C=C}$, TBI is stronger. The data from photoelectronic spectroscopy[9] and different quantum-chemical methods[6,7] exactly point to this sequence of higher occupied π-orbitals in structure **1**.

In order to estimate the possibility of the influence of electronic interactions between double bonds on the flexibility of the 1,4-cyclohexadiene ring we calculated the energy characteristics of molecule **1** at different bending angles using the AM1 method[10] with full optimization of geometry. The values of TBI and TSI were estimated from the expansion of the full electronic energy in terms of one- and two-electron contributions, using the following equation in a Hartree—Fock approximation:

$$E^{\mathrm{el}} = \mathrm{Tr}\,\rho h^{\mathrm{ad}} = \sum_{i} \|\rho h^{\mathrm{ad}}\|_{ii} = \sum_{i}\sum_{j} \rho_{ij}\, h^{\mathrm{ad}}_{ji} = \sum_{i,j} \|E^{\mathrm{el}}\|_{ij},$$

$$h^{\mathrm{ad}} = h + 0.5G,$$

where ρ is the matrix of the charge density, and the summation is carried out only of two-electron contributions from the appropriate p_z-AO. The results of the calculations are presented in Table 1.

Table 1. The dependence of the total energy of the molecule and energies of TSI and TBI on the angle between planes of double bonds

φ/deg	E_{TSI}/eV	E_{TBI}/eV	E_{Σ}/kcal mol^{-1}
180	−0.0028	−1.46	0
175	−0.0027	−1.43	0.04
170	−0.0024	−1.34	0.16
165	−0.0020	−1.22	0.34
160	−0.0015	−1.08	0.63

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From the data of Table 1 it follows that a decrease in the angle between the planes of the double bonds brings about significant attenuation of TBI, whereas TSI is little affected. Since the through-bond interaction is greatest in the flat conformation, it is a supplementary flattening factor, and, in parallel with steric effects, has significant influence on the equilibrium structure and conformational flexibility of the 1,4-cyclohexadiene molecule.

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Monoamination of internal fluoroolefins

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Perfluoro-2-methyl-2-pentene and perfluoro-1-methylcyclopentene react with ammonia or aniline under controlled conditions to give monoamination products.

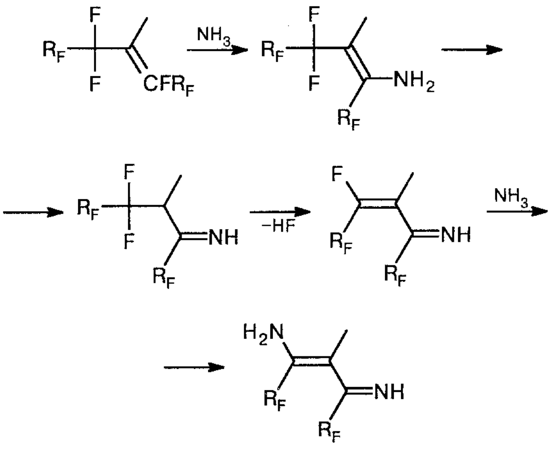
Key words: internal fluoroolefins, amination; fluorinated enamines, fluorinated imines, synthesis.

Reactions of internal fluoroolefins with ammonia usually occur as vinylic substitution followed by enamine-imine isomerization and dehydrofluorination giving rise to imino-enamines (**1**) or the products of their further transformations[1–4] (Scheme 1).

The products of the monoamination of perfluoro-2-butene or isomeric C_8F_{16}-olefins by ammonia have also been reported.[5,6]

We found that perfluoro-2-methyl-2-pentene (**2**) also gives a monosubstituted product, *viz.*, imine **3a**, in a moderate yield under controlled conditions (0—20 °C, calculated amount of ammonia). Similarly, anil **3b** and enamine **5** were prepared from olefin **2** and aniline or

Scheme 1



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