Computational study of small heteraphanes

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ABSTRACT

Electronic structure calculations of [2.2](2,5)- and [2.2.2.2](2,3,4,5)heteraphanes have been performed using double hybrid Density Functional Theory (DFT) with dispersion correction. The total strain energies and their components in these heteraphanes have also been estimated.

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1. Introduction

Cyclophanes (CP) are interesting to chemists for two main reasons, one conceptual the other practical.

Firstly, CP molecules often exhibit intramolecular strain with subsequent changes in the aromaticity of aromatic rings (if present) and also furnish a molecular skeleton which facilitates π–π electron interactions between aromatic rings. Secondly, CP have multiple practical applications e.g. as components of chiral catalysts, as materials for photonics and optoelectronics and as guests for recognition of biomolecules [1–5].

The CPs with more than one aromatic ring provide a good case study for analyzing the interplay of inter-ring (trans-annular) interactions, aromatic ring distortions and the influence of ethylene bridges on the CP structure and stability. Numerous reports in the literature described the nature of intramolecular interactions in CP, but they were not always concordant with each other. Some reports suggested that the transannular interactions in archetypal CP [2.2]paracylophane do not exist [6] while other studies have stressed the need for using correlated *ab initio* quantum chemical methods with large basis sets to arrive at the correct description of such interactions [7].

In this work I have selected two classes of molecules in which the aforementioned intramolecular interactions can be expected to be more pronounced than in the other CPs reported to date. These classes are shown in Scheme 1 and comprise series of [2.2](2,5)heteraphanes (**II**) and [2.2.2.2](2,3,4,5)heteraphanes (**I**). These heteraphanes are unknown with the exception of oxa and thio derivatives whose molecular structures were determined by

X-ray diffraction [8,9]. The experimentally determined structures can serve as an independent check on the accuracy and reliability of theoretical methods employed in this work.

2. Computational methods

The quantum chemical calculations were performed with Gaussian 09 program [10]. The calculations included full geometry optimization of neutral molecules using ωB97XD density functional which contains dispersion corrections and the 6-311G basis set. The vibrational analysis performed confirmed that the optimized geometries were true minima on potential energy surfaces (no imaginary frequencies). The need to take into account long range intramolecular dispersion interactions in CPs had been recognized previously [11,12]. The comparison of calculated and experimental (where available) geometries of heteraphanes is given in Table 1. The calculated geometries are in good agreement with the experimental values except for the C—O bond length in [2.2](2,5)-furanophane. The experimental C—O bond length in [2.2](2,5)furanophane is 1.392 Å, which appears to be too long. This bond length is not only much larger than the calculated value, but is also too large when compared to the C—O bond length in furan which is 1.3641 Å [13]. The good agreement between the calculated and experimental geometries gives confidence in the reliability of conclusions drawn from the computational results. All calculations included un-scaled zero-point energy (ZPE) correction.

3. Results and discussion

The calculated energies and geometries of heteraphane molecules in series **I** and **II** are presented in Tables 1 and 2 and explained in Scheme 2.

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Table 1
Some calculated (ωB97XD/6-311G∗) geometry parameters: distances (d/Å) and angles (deg) for CP[a,b].

X	$<X_{tw}$	$<$ethyl	d_{XX}	$d_{22'}$	$d_{33'}$	d_{CX}	$d_{C=C}$	d_{C-C}	$<$interpl
[2.2.2.2](2,3,4,5)Heteraphanes C_2 symmetry									
BH	7.5	13.5	3.040	2.729	2.636	1.582	1.344	1.533	3.9
CH₂	12.1	14.0	3.225	2.750	2.631	1.508	1.347	1.483	5.2
PH	20.5	12.0	3.592	2.791	2.633	1.836	1.349	1.484	7.1
O	4.1	9.3	2.834	2.685	2.631	1.361	1.359	1.442	2.4
NH	4.3	0.0	2.890	2.724	2.640	1.374	1.376	1.431	3.7
Se	11.1	11.5	3.514	2.809	2.642	1.883	1.360	1.451	7.7
SiH₂	18.1	17.6	3.749	2.797	2.642	1.874	1.349	1.513	7.0
S	9.3	9.6	3.316	2.785	2.635	1.740	1.364	1.443	6.8
Exp	8.6		3.244	2.757	2.598	1.723	1.368	1.447	7.2
[2.2](2,5)Heteraphanes C_{2h} symmetry									
X	$<X_{tw}$	$<$ethyl	d_{XX}	$d_{22'}$		d_{CX}	$d_{C=C}$	d_{C-C}	$d_{interpl}$
BH	17.0	25.9	2.639	2.654		1.580	1.342	1.518	2.08
CH₂	15.3	38.9	2.931	2.873		1.503	1.349	1.474	2.43
PH	26.2	31.3	3.977	2.862		1.809	1.355	1.465	2.66
O	6.1	51.6	2.493	2.911		1.357	1.357	1.434	2.32
Exp[b]	5.9	50.7	2.511			1.392	1.351	1.451	2.34
NH	6.6	47.0	2.655	2.871		1.371	1.377	1.427	2.47
Se	13.2	30.4	3.706	2.909		1.876	1.361	1.437	2.72
SiH₂	22.6	13.0	3.938	2.734		1.882	1.344	1.491	2.61
S	10.4	35.7	3.321	2.889		1.732	1.366	1.430	2.66
Exp	9.5	34.4	3.225			1.728	1.369	1.435	2.63

[a] $d_{22'}$ and $d_{33'}$ indicate distances between α and β-carbons of the two five-member rings, respectively.
[b] The value of C—O bond length in [2.2](2,5)furanophane [8] seems suspect not only because of discrepancy with the calculated DFT geometry, but also when compared to the C—O length of furan itself [13].
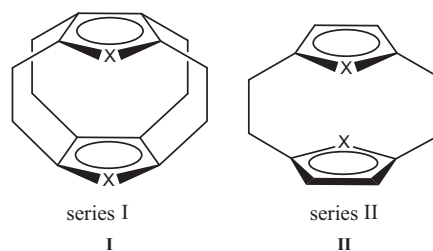
Table 2
Strain energy and its components (kJ/mol) for heteraphanes[a,b].

X	$\Delta E_{interact}$	ΔE_{ring}	$-\Delta E_{ethyl}$	SE
[2.2.2.2](2,3,4,5)Heteraphanes				
BH	136.83	122.21	−56.60	202.44
CH₂	139.4	139.54	−65.47	213.46
SiH₂	125.92	123.93	−45.36	204.50
NH	151.97	110.59	−54.84	207.72
PH	130.80	128.62	−46.81	212.60
O	152.47	126.6	−65.3	213.76
S	143.21	126.26	−49.09	220.39
Se	138.83	123.31	−40.72	221.43
[2.2](2,5)Heteraphanes				
BH	32.44	66.73	−44.73	54.43
CH₂	38.84	102.87	−38.71	103.0
SiH₂	41.61	106.46	−10.17	137.90
NH	11.95	73.14	−41.04	44.06
PH	48.56	119.49	−19.98	148.07
O	39.58	57.95	−33.07	64.46
S	62.02	95.43	−22.28	135.18
Se	66.75	105.87	−13.52	159.09
Cyclophanes				
Para-CP[c]	59.8	92.9	−26.4	126.4
Meta-CP[c]	42.3	50.6	−46.4	46.4

[a] Components are: ΔE_{ring} = total bending strain of both rings; $\Delta E_{interact}$ = through-space interaction between rings; ΔE_{ethyl} = strain of ethylene bridges.
[b] $\Delta E_{ethy} = \Delta E_{alk} + \Delta E_{dealk}$.

Scheme 1. structures of heteraphanes of series **I** and **II** (hydrogens are omitted for clarity); X = BH, CH₂, SiH₂, NH, PH, O, S, Se.

The data obtained provided interesting insights. One of the main characteristics of the heteraphanes in series **I** and **II** is that they are strained molecules. The strain energy (SE) can be assumed to comprise three main components: the repulsive (destabilizing) interaction between π-electron densities on the heterocyclic rings ($\Delta E_{interact}$), the deformation of heterocyclic rings and their exocyclic bonds (ΔE_{ring}) and the deformation of ethylene bridges which join the heterocyclic rings together (ΔE_{ethane}). I have used the thermochemical cycles shown in Scheme 2 to estimate values of SE and its components (Table 2). Heteraphanes **II** have smaller SE values than their series **I** counterparts which can be expected due to the larger number of ethylene bridges in the latter series. The heteraphanes containing X = BH groups have the smallest and those with X = Se the largest SE values. For heteraphanes which contain heteroatoms from the same group of the periodic table, the larger the size of the X group the larger the SE value. The borolophane derivative (X = BH) has the smallest SE value in series **I** which can be expected due the electron deficient character of the BH group; this character reduces the net electron density repulsion between BH groups.

However, an interesting observation is that relative size of the X group (influenced by the heteroatom size and the presence or absence of hydrogens attached to it) is not the only factor influencing SE. For example, the SE energies of CPs with X = BH and X = SiH₂ groups in series **I** differ by only 2 kJ/mol in spite of large difference in the sizes of their respective X groups (Table 2). This similarity of SE values can be rationalized by inspecting the molecular structure data in Table 1. The larger size of SiH₂ group is accommodated by increasing the twist angle ($<X_{tw}$) and the interplanar angle ($<$interplanar) on going from BH to SiH₂ derivative. The SE values in series **II** generally span much larger range of values than their analogues in series **I**. This is consistent with lesser conformational rigidity of molecules in series **II** vs. series **I**. Conformational rigidity of the molecule forces parts of the molecule to come closer together thus