
Theoretical Description of Aromaticity in Superphane Cages

N. MIRELES, R. SALCEDO, L. E. SANSORES, A. MARTÍNEZ

Instituto de Investigaciones en Materiales, UNAM, Apartado Postal 70-360, Circuito Exterior, Ciudad Universitaria, México DF 04510, México

Received 24 January 2000; revised 1 June 2000; accepted 2 June 2000

ABSTRACT: We study the family of superphanes that are formed by two rings with bridges connecting the carbon atoms in neighboring ring, which result in the shape of a cage. We have considered from 3 to 7 member rings. The superphanes are charged so as to make them aromatic or antiaromatic. All calculations were done with the Gaussian 94 code at the B3LYP/6-31G** level. In all cases the geometry was optimized. The magnetic properties were also calculated at this level using the continuous set of gauge transformation method. The form of the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) indicate that they should show the transannular phenomena. NICS are reported and used to analyze the aromatic character. © 2000 John Wiley & Sons, Inc. *Int J Quantum Chem* 80: 258–263, 2000

Key words: superphanes; cyclophanes; aromaticity; transannular phenomena

Introduction

Superphanes that are constituted by rings connected by aliphatic bridges have been synthesized and describe elsewhere [1, 2]. The classical [2₆](1,2,3,4,5,6) cyclophane (compound **3**) is the best example of this kind of molecule. It is possible to design a collection of these molecules with different ring sizes or various bridge lengths. In Fig-

ure 1 a set of these superphanes are shown, with ring sizes ranging from 3 to 7 member rings.

Of this family, only compound **3** has been synthesized and characterized by X-ray diffraction analysis [3, 4]. It is highly symmetrical, D_{6h} , and the rings are in a eclipsed conformation, with the planar regular benzene rings separated by 2.624 Å. Photoelectron spectroscopy of this compound has also been reported [3, 5]. It was shown that through-space and through-bond interactions are important to understand the splitting of the benzene molecular orbitals (MOs); the first ionization energy of 7.55 eV is a low value for the [2_n] cyclophanes.

Linder in 1976 using a π -SCF (self-consistent field) force field method [6] predicted the geometry for compound **3**. The interaction between the rings in these systems means that the π orbitals are not

Correspondence to: L. E. Sansores.

Contract grant sponsor: CONACYT.

Contract grant number: 3157PA.

Contract grant sponsor: UNAM.

Contract grant number: IN101597.

Contract grant sponsor: Dirección General de Asuntos del Personal Académico.

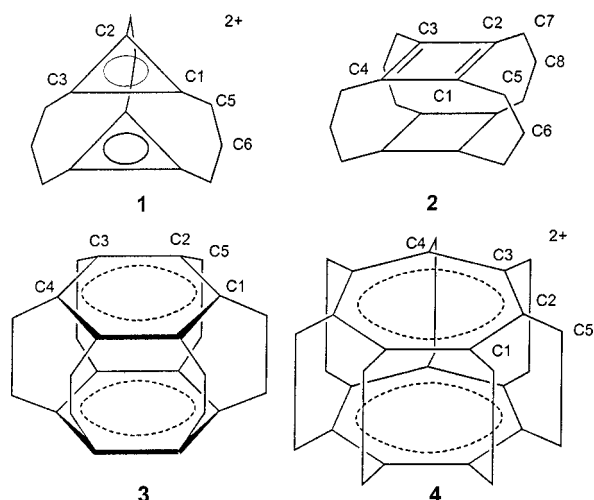


FIGURE 1. Compounds under study: **1** is $[3_3](1, 2, 3)$ cyclophane $^{2+}$, **2** is $[3_4](1, 2, 3, 4)$ cyclophane, **3** is $[2_6](1, 2, 3, 4, 5, 6)$ cyclophane, and **4** is $[2_7](1, 2, 3, 4, 5, 6, 7)$ cyclophane $^{2+}$. The prime notation referred to in the text indicate the same position in the lower ring.

perpendicular to the ring plane and that there is a repulsion between the π orbitals.

Attempts to synthesize $[3_3](1, 2, 3)$ cyclophane (compound **1**) have only given the $[3_3](1, 2)$ cyclophane [7]. Nevertheless, new synthesis techniques indicate that its synthesis will probably occur soon. It is possible to synthesize $(\text{CoCp})_2[n_4](1, 2, 3, 4)$ cyclophane where the CoCp are attached to both rings [8, 9]. Oxidation of this compound with Ce^{IV} removes the CoCp and probably generates compound **2**, which immediately rearranges by an intramolecular Diels–Adler reaction [1, 10]. X-ray characterization of the $(\text{CoCp})_2[n_4](1, 2, 3, 4)$ cyclophane [8] shows that the four member rings are planar, parallel with each other, and that all bonds on the rings are 1.454 Å long. The distance between the rings is 2.944 Å.

The main feature to study that can yield interesting results is the presence of aromatic or antiaromatic fragments; many of the molecules characteristics can be seen from the viewpoint of aromaticity, for example, transannularity effects, reactivity, interaction with metals, etc. In this work the charge on the compounds has been adjusted so as to make the rings aromatic or antiaromatic and restricted to the dications and uncharged species.

The main aim of this work develops a systematic study, based on the aromatic behavior of some symmetrical superphanes made from cyclic moieties. Theoretical calculations at ab initio level have

been carried out on the set of molecules shown in Figure 1. An analysis of the aromaticity of these compounds was carried out in order to study stability, delocalization pathways, and through-space and through-bond effects.

All calculations were done with the Gaussian 94 code [11] at the B3LYP/6-31G** level. In all cases the geometry was optimized. The magnetic properties were also calculated at this level using the continuous set of gauge transformation method [12].

Results

GEOMETRICAL CONSIDERATIONS

The optimized structures can be seen in Figure 1. In general, the behavior is very similar for all of them, i.e., the rings are flat and parallel to each other.

The $[3_3](1, 2, 3)$ cyclophane dication, compound **1**, has a C_{3h} symmetry with the base and top rings parallel and completely regular. The bond lengths and angles are summarized in Table I. The bond length in the ring is 1.380 Å, which is short for a single bond and long for a double bond, indicating that there is electron delocalization in the ring. The bond lengths in the side chains correspond to those of single bonds. The bond angles in the side chains are distorted with respect to those expected for an sp^3 hybridization.

The $[3_4](1, 2, 3, 4)$ cyclophane, compound **2**, has symmetry C_{2h} , with the four member rings having the form of rectangles with sides 1.347 and 1.587 Å; these bond lengths indicate that there is no electron delocalization; two bonds are single and two are double. The rings are completely flat and parallel to each other; see Table II. The side chains are also equal in opposite pairs, but the bond lengths of all

TABLE I
Bond lengths and angles for $[3_3](1, 2, 3)$ cyclophane, compound **1**.

Bond	Length (Å)	Angles	Angle (deg.)
C1–C2	1.380	C1–C2–C3	60.0
C1–C5	1.483	C2–C1–C5	148.4
C5–C6	1.558	C3–C1–C5	150.0
Ring1–Ring2	3.029	C1–C5–C6	112.2
		C5–C6–C5'	116.5
		C1–C2–C2'–C1'	0.0
		Ring1–Ring2	0.0

TABLE II
Bond lengths and angles for [3₄](1, 2, 3, 4)
cyclophane, compound 2.

Bond	Length (Å)	Angles	Angle (deg.)
C1–C2	1.341	C1–C2–C3	90.3
C2–C3	1.587	C2–C3–C4	89.7
C1–C5	1.490	C2–C1–C5	136.2
C5–C6	1.552	C4–C1–C5	132.4
C2–C7	1.501	C1–C5–C6	114.5
C7–C8	1.550	C5–C6–C5'	116.8
Ring1–Ring2	3.068	C1–C2–C7	133.4
		C3–C2–C7	135.8
		C2–C7–C8	115.3
		C7–C8–C7'	117.1
		C1–C2–C3–C4	0.0
		C1–C2–C2'–C1'	0.0
		Ring1–Ring2	0.1

four chains correspond to single bonds. The bond angles in the side chains are again distorted with respect to those of an sp^3 hybridization. This result is different from what is found in (CoCp)₂[*n*₄](1, 2, 3, 4) cyclophane [8] since in this compound the four-member ring has all four sides of equal length. This is probably due to the type of bonding between the Co and the cyclobutadiene that improves the development of aromaticity of the rings with an associated delocalization of electrons. Additionally the ring–ring distance is bigger in our calculations than that reported for that (CoCp)₂[*n*₄](1, 2, 3, 4) cyclophane.

The [2₆](1, 2, 3, 4, 5, 6) cyclophane, compound 3, has D_6 symmetry. The bond lengths and angles are given in Table III. The rings are completely flat

TABLE III
Bond lengths and angles for the [2₆](1, 2, 3, 4, 5, 6) cyclophane, compound 3.

Bond	Length (Å)	Exp. ^a	Angles	Angle (deg.)
C1–C2	1.414	1.406	C1–C2–C3	120.0
C2–C5	1.523	1.518	C1–C2–C5	117.9
C5–C5'	1.606	1.580	C3–C2–C5	118.0
Ring1–Ring2	2.663	2.624	C2–C5–C5'	110.3
			C1–C2–C3–C4	0.0
			C1–C2–C2'–C1'	–0.4
			Ring1–Ring2	0.0

^a A. W. Hanson, T. S. Cameron, *J. Chem. Res. Symp.* 336, 1980, 336–337.

TABLE IV
Bond lengths and angles for the [2₇](1, 2, 3, 4, 5, 6, 7)
cyclophane, compound 4.

Bond	Length (Å)	Angles	Angle (deg.)
C1–C2	1.414	C1–C2–C3	128.6
C2–C5	1.544	C1–C2–C5	114.0
C5–C5'	1.607	C3–C2–C5	114.4
Ring1–Ring2	2.602	C2–C5–C5'	108.6
		C1–C2–C3–C4	0.0
		C1–C2–C2'–C1'	4.0
		Ring1–Ring2	0.0

and parallel to each other, but the bottom ring is slightly rotated, by -0.4° , with respect to the top ring. The C–C bond length in the ring is 1.414 Å indicating electron delocalization. The bond lengths of the side chains correspond to single bonds, however, the bonding between C5–C5' is fairly long, 1.62 Å. The calculated bond lengths are slightly bigger than those obtained experimentally. This is to be expected since our calculations are in the gas phase and experiments are done in the solid phase [4].

The [2₇](1, 2, 3, 4, 5, 6, 7) cyclophane dication, compound 5, has D_7 symmetry, and its characteristics are very similar to those of compound 3—the rings are flat and parallel with the bottom ring slightly rotated by 4° from the eclipse position. The C–C bond length in the ring is 1.414 Å, again indicating electronic delocalization. The bond lengths in the side chains correspond to single bonds, and the vertical bond (C5–C5') is also fairly stretched at 1.607 Å. The bond lengths and angles are summarized in Table IV.

ELECTRONIC STRUCTURE

Figure 2 shows the spatial representation for the lowest unoccupied and highest occupied molecular orbitals: LUMO, HOMO, HOMO-1 and HOMO-2 of compounds 1–4. In Table V the energies of the LUMO and HOMO orbitals are given.

In these compounds the LUMO shows a direct interaction between the two rings, indicating transannular effects. In compounds 1, 3, and 4 the LUMO forms a tubelike structure. The HOMOs of compounds 1, 3, and 4 are ring shaped from the π contributions of the carbons on the rings, indicat-

ing delocalization of the electrons. Compound 2 is different since, as is well known, the cyclobutadiene is antiaromatic and does not give delocalization on the rings; the HOMO is located on the short bonds of the four member rings, while the LUMO is on the long bonds. In compound 1, HOMO-1 and HOMO-2 correspond to σ orbitals, while in the other compounds the HOMO-1 also has interaction between the upper and lower rings. The behavior of HOMO-2 is different for each compound.

The behavior of the gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) does not show a trend, the smallest gap is for compound 2, indicating that it has the highest reactivity,

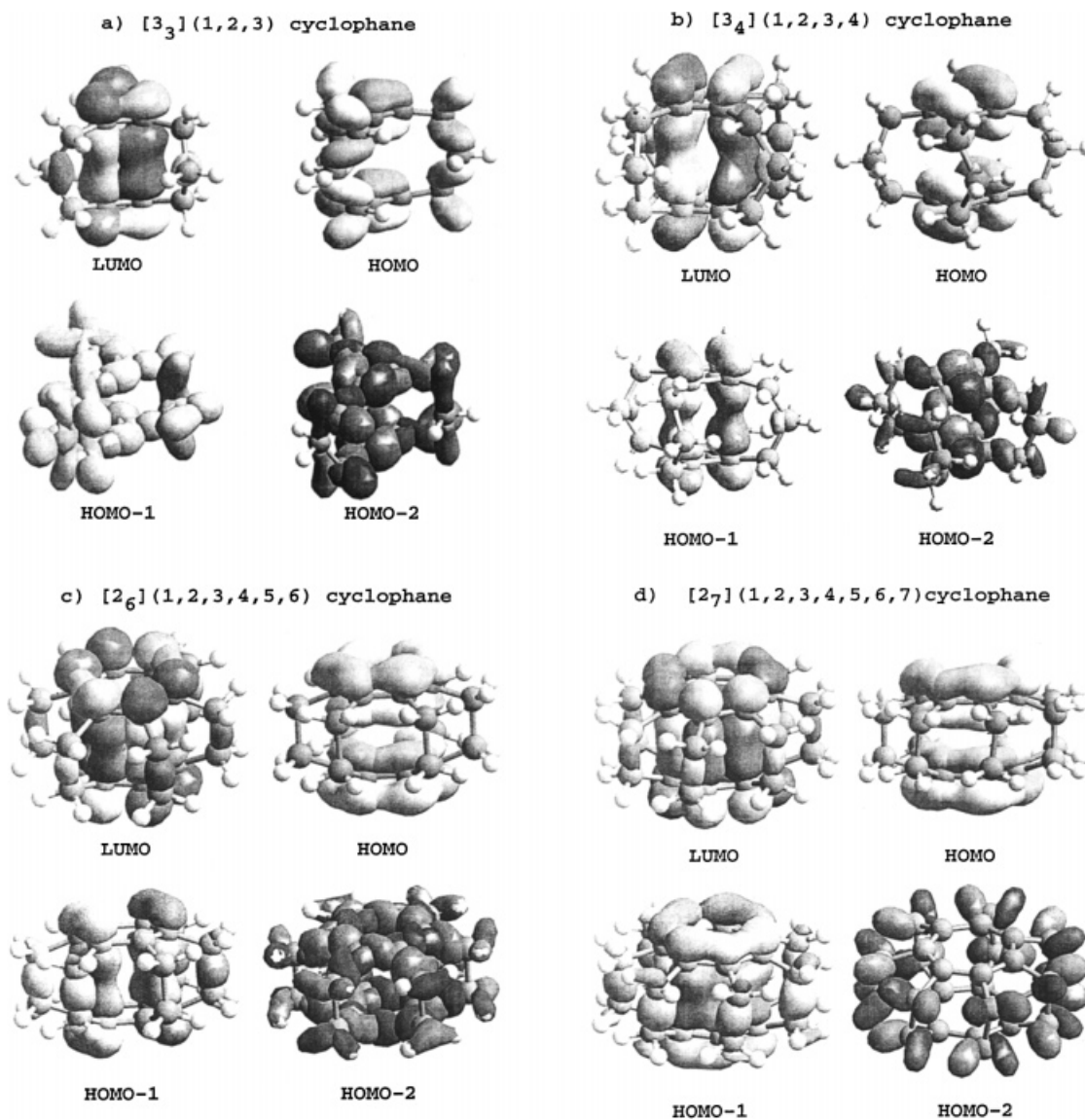


FIGURE 2. Spatial representation of the LUMO, HOMO, HOMO-1, and HOMO-2 of the compounds under study: (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4.

TABLE V

Total energy (E_T), energy of the HOMO (E_{HOMO}), energy of the LUMO (E_{LUMO}), gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), total charge of the compound, and dipole moment for the compounds under study.

Compound	1	2	3	4
E_T (hartree)	-581.73669	-776.37851	-928.94915	-1069.82300
E_{HOMO} (eV)	-16.506	-3.475	-5.566	-16.400
E_{LUMO} (eV)	-9.788	-1.290	-0.052	-6.755
ΔE (eV)	6.718	2.185	5.514	9.645
Total charge	2.0	0.0	0.0	2.0
Dipole (D)	0.0	0.0	0.0	0.0

while the largest gap is that of compound **4**. Table VI gives the charges as obtained from a Mülliken analysis. In all cases the carbons on the side chains are negatively charged; and those rings are positively charged; however, the dipole moments are zero in all cases.

The transannular effect has been studied for the [2,2]paracyclophane [13]. It was established that the phenomenon arises mainly from a through-space pathway (i.e., the contribution through bond pathway is minimal). This behavior is followed in these compounds. Considering that we have more branches in the superphanes, an important contribution could be expected from the lateral saturated bridges to the wave function of the frontier orbitals—this is not the case. The main contributions arises from the π - π interactions between both rings.

It has been demonstrated that [2,2]paracyclophane is more reactive toward metals and organometallic fragments than *p*-xylene [13, 14]. This behavior is due to the presence of the transannular effect. The π - π repulsion between the rings increases the electron density in the outer faces of the ligand with a concomitant increase of the nucleophilicity relative to benzene. This behavior is

TABLE VI

Charges of the atoms in the compounds as obtained from a Mülliken analysis.

Compound	1	2	3	4
C1	0.1532	0.0345	0.0443	0.0214
C2	0.1532	0.0584	0.0443	0.0214
C5	-0.2975	-0.2528	-0.2406	-0.4737
C6	-0.2372	-0.1637		
C7		-0.2471		
C8		-0.1855		

present in all compounds; all of them show the transannular effect and a suitable nucleophilic orbital (LUMO) for interaction with metals.

MAGNETIC PROPERTIES

The magnetic susceptibilities for compounds **1** through **3** have been calculated and are summarized in Table VII. To calculate the nuclear independent center susceptibility (NICS), we followed the technique developed by Schleyer [15], a ghost atom was located at the center of each ring and at the geometrical center of the cage, and the magnetic susceptibility was calculated at this positions. The NICS are reported in Table VII (NICS1 at the center of the ring, NICS2 at the center of the compound). In all compounds susceptibilities at the C on the rings are much lower than those of the carbon atoms on the side chains. This is due to different hybridization, carbon atoms on the rings have an sp^2 hybridization

TABLE VII

Isotropic magnetic susceptibilities at atom positions χ_{C1} , χ_{C2} , χ_{C5} , χ_{C6} , χ_{C7} , and χ_{C8} , total isotropic magnetic susceptibility χ_{TOTAL} , and calculated NICS.

Compound ^a	1	2	3
χ_{C1} (ppm)	7.95	44.3	46.1
χ_{C2} (ppm)	7.95	47.4	46.1
χ_{C5} (ppm)	164.7	163.1	158.0
χ_{C6} (ppm)	172.0	176.6	
χ_{C7} (ppm)		165.3	
χ_{C8} (ppm)		162.5	
χ_{TOTAL} (ppm)	-100.0	-119.4	-195.9
NICS1 (ppm)	-18.3	22.0	-13.4
NICS2 (ppm)	-6.29	14.7	-19.7

^a NICS1 is at the center of one of the rings and NICS2 at the center of the compound.

while carbon atoms on the side chain are sp^3 . This is also indicative of electron delocalization. Negative NICS are indicative of an aromatic behavior, and thus compounds **1** and **3** have an aromatic behavior, while compound **2** has an antiaromatic one. The rings of the same compounds have similar behavior. Compound **2** has positive NICS both for the molecule as a whole and for the rings, which means that this compound has an antiaromatic behavior as expected from the presence of the cyclobutadiene. This high antiaromatic character indicates that compound **2** is very unstable; thus it should be very difficult to obtain in agreement with the experimental observations [10].

In compound **3**, the NICS at the center is bigger than that at the center of the ring, indicating that the transannular effect is very strong giving an aromatic character to the whole molecule. Compounds **1** and **2** have longer side chains, and as the chain size increases the transannular effect should diminish, allowing more electron delocalization on the rings. This is indicated by bigger NICS at the rings than at the center.

Compound **3** is an excellent candidate to attach a metal atom inside the cage because of the electronic delocalization at the central point. However, the electronic repulsion can compel the metal to react on one of the faces and complexes, as those reported with Cr and Ru [16–18] would be expected.

Conclusions

It has been shown that superphane cages with up to seven member rings have highly symmetric structures. As we move away from the rings, the bond lengths in the side chains increase, this being a consequence of the high electron delocalization. The electron delocalization is not only on the rings but in the whole molecule, as indicated by the direct interaction between the rings. This delocalization gives rise to the transannular effect, where charges can be transferred from one ring to the other. NICS value indicates that the molecules as a whole behave with an aromatic or antiaromatic character following Hückel's law of $4n + 2 \pi$ electrons.

ACKNOWLEDGMENTS

We thank CONACYT (grant 3157PA) and Dirección General de Asuntos del Personal Académico,

UNAM (grant IN101597) for financial support. We would like to acknowledge the Dirección General de Computo Académico at UNAM for providing computer time.

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