## The Computed Aromaticity of the Tetra-Substituted Cyclobutadiene Ring in Various Complexes

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The paper presents the results of computations regarding the aromaticity of the tetra-substituted cyclobutadiene ring in  $[Z_4C]L$  type complexes, using TOPAZ algorithm. There are no "double" bonds in the tetra-substituted cyclobutadiene ring in the analyzed complexes. The substituents Z = -CO-R ( $R = H, CH_3$ , OH, OCH\_3) increase the aromaticity more than Z = -O-R ( $R = H, CH_3$ , Ph) substituents. The ligands  $L = PdCl_2$  and  $L = Fe(CO)_3$  increase the aromaticity more than other analyzed ligands. The influence of Mo(CO)\_4 ligand is ambiguous. The complexes Z = H;  $L = Mo(CO)_4$  and Z = COOH;  $L = PdCl_2$  present the largest computed aromaticity of the cyclobutadiene ring ( $A \sim 242$  when  $A_2 = -1000$ ). In addition, in the complexes where  $L = Fe(CO)_3$  all C - L bonds are computed as "coordinative"; on the contrary, in the complexes where Z = H,  $CH_3$ ,  $C(CH_3)_3$ ,  $Si(CH_3)_3$ ,  $Ph; L = NiCl_2$ ,  $PtCl_2$  all C - L bonds are computed as "single". In dimers of  $[Z_4C]L$  complexes the aromaticity of the cyclobutadiene ring (S) seems to be larger.

Keywords: cyclobutadiene complexes, aromaticity, TOPAZ algorithm

In 1931, Hückel described a very simple approach to the  $\pi$ -electronic structure of planar molecules [1]. According to the Hückel model cyclobutadiene is "antiaromatic" because its ring has 4  $\pi$ -electrons, and 4 is not the double of an odd number.

Cyclobutadiene is very unstable and has been observed only as a matrix-isolated species, trapped in a frozen inert gas [2]. In contrast to the square geometry predicted by Hückel theory this molecule has a rectangular structure, verified by infrared studies [3].

Higgins, Orgel and others suggested [4-8] that, despite its instability, cyclobutadiene might be able to form stable complexes because the metal atom provides two more electrons to the system. Few years later the synthesis of certain cyclobutadiene complexes was achieved [9-12]. Moreover, the synthesis of some derivatives by electrophilic substitution [13] offered a "chemical" proof for the aromaticity of the complexed cyclobutadiene ring. In present, the literature is flooded by papers regarding substituted complexed cyclobutadiene [14-26].

This paper presents the results of the computations regarding the aromaticity of the tetra-substituted cyclobutadiene ring in various complexes. Therefore, one can observe the (calculated) influence of the substituent and ligand chemical structure on the aromaticity of the cyclobutadiene ring.

## **Experimental part**

Methods

We analyzed the  $[Z_4C]L$  type complexes, where Z is the substituent, C is the cyclobutadiene ring and L is the ligand.

In order to obtain the results presented below, we have optimized the molecular geometries using the MMX [27] method (included in PCModel [28] molecular mechanics program) and then, more rigorously, by PM6 [29] method (included in MOPAC [30] quantum mechanics program). The MOPAC program used the keywords "pm6 pulay gnorm=0.2 geo-ok bonds". The geometry optimization must be sufficiently correct because the geometry influences the calculated values of the bond orders and aromaticity.

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Based on the results obtained using the PM6 method one can consider:

- the "coordinative" bond is the bond having a bond order within range (0.100, 0.050)

- the "single" bond is the bond having a bond order within range (0.500, 1.051)

- the "aromatic" bond is the bond having a bond order within range (1.051, 1.851)

- the "double" bond is the bond having a bond order within range (1.851, 2.500)

The above limit values of the bond order were used in evaluation of aromaticity by DESCRIPT program [31], according to TOPAZ algorithm [32], parameterized to use the PM6 method.

According to TOPAZ algorithm the computed aromaticity is within range [-1000, +1000]. If the computed aromaticity is within range [-1000, -350] the ring is "antiaromatic". If the computed aromaticity is within range [-350, 0] the ring is "non-aromatic". If the computed aromaticity is within range [0, 1000] the ring is "aromatic". In fact, cyclobutadiene presents the smallest computed aromaticity (i.e. -1000) and benzene the largest aromaticity (i.e. +1000).

In addition, according to the TOPAZ algorithm, some "non-aromatic" rings are "alternant" structures (alternanting "single" and "very low aromatic" bonds). Other "non-aromatic" rings are "non-alternant" structures because they present a "discontinuous conjugation" (two or more adjacent "single" bonds).

## **Commented results**

The table includes the computed aromaticity of the tetra-substituted cyclobutadiene ring in many complexes, some of which have not yet been synthesized.

There are no "double" bonds in the tetra-substituted cyclobutadiene ring in the analyzed complexes. The cyclobutadiene ring computed as "aromatic" includes two "single" bonds and two "aromatic" bonds ("alternant" structure). The cyclobutadiene ring computed as "nonaromatic" is either an "alternant" structure (including "single" and "very low aromatic" bonds) or a "non-

Substituent Z	Ligand L	Aromaticity	Substituent Z	Ligand L	Aromaticity
Н	PdCl <sub>2</sub>	196	СООН	PtCl <sub>2</sub>	33
н	NiCl <sub>2</sub>	155	соон	Fe(CO) <sub>1</sub>	158
H ·	PtCl <sub>2</sub>	78	COOH	Mo(CO)4	84
н	Fe(CO) <sub>3</sub>	154	OCH	PdCl <sub>2</sub>	-2
ਸ	Mo(CO) <sub>4</sub>	243	OCH <sub>3</sub>	NiCla	-12
н	Co(Cp')	137	OCH <sub>3</sub>	Fe(CO) <sub>3</sub>	35
CH <sub>3</sub>	PdCl	205	SCH <sub>3</sub>	PdCl	161
CH <sub>3</sub>	NiCla	92	SCH	NiCla	53
CH	PtCl <sub>2</sub>	36	SCH <sub>3</sub>	PtCI <sub>2</sub>	-9
CH <sub>3</sub>	Fe(CO) <sub>3</sub>	58	SCH <sub>3</sub>	Fe(CO) <sub>b</sub>	216
CIL	Mo(CO) <sub>4</sub>	232	SCH	MorCOl	11
CH <sub>1</sub>	Co(Cp)	93	N(CH <sub>3</sub> ) <sub>2</sub>	PdCL	48
C(CH <sub>1</sub> ) <sub>1</sub>	PdCb	219	N(CH <sub>4</sub> ) <sub>2</sub>	NiCb	-6
C(CH <sub>1</sub> ),	NiCh	96	N(CH <sub>2</sub> )	Fe(CO)	18
C(CHa)	PtCL	39	N(CH <sub>4</sub> ) <sub>2</sub>	Mo(CO)4	108
C(CH <sub>1</sub> )	Fe(CO)	90	Ph	PdCb	182
$C(CH_2)_2$	Mo(CO)	200	Ph	NiCh	78
C(CHa)	Co(Cn)	105	РЪ	PtCl	20
Si(CIL)	PdCl	181	թե	Fe(CO)	186
SI(CH-)	NiCh	85	РЪ	Mo(CO)	21
Si(CH <sub>2</sub> )	PtCl.	36	OPh	PdCl.	31
SuCHa	Fe(CO)	90	OPh	NiCh	-9
Si(CIL)	Ru(CO)	69	OPh	Fe(CO)	-2
Si(CIL)	Mo(CO)	201	SPh	PdCla	64
Si(CH <sub>2</sub> ) <sub>2</sub>	Co(Cp)	84	SPh	NICL	41
OH	NiCh	DC"	SPh	PtCl	-6
OII	P(Cla	DC	SPh	FerCOb	196
0H	Fe(COb	DC	SPh	Mo(CO)	99
OU	Mo(CO)	DC	N(Ph)a	PdCla	58
SH	PdCb	108	N(Ph) <sub>2</sub>	NiCla	-26
SH	NiCh	27	COCH	PdCla	222
SH	Fe(CO)	212	COCH	NiCl	101
NH	PdCla	19	COCIL	PICIa	40
NH <sub>2</sub>	NiCla	-14	СОСН	Fe(COb	190
NHa	Ec(CO)	58	COCU	MatCO	97
CHO	PdFs	146	COOCH	PdCb	169
CHO	PdCL	738	COOCH	NiCh	78
CHO	PdBr.	199	COOCH	PtC1.	16
CHO	PdL.	1/18	COOCH	FatCOL	175
CHO	NiCla	00	COOCH	Marcon	97
CHO	PrCl.	32	NO.	NICL.	67
CHO	FelCOL	165	NO	PtCL.	7
CHO	Mo(CO).	105	NO.	$F_{\alpha}(C\Omega)$	118
COOH	Pach.	241	NO.	MatCON	68
СООН	DdBra	103		NGCU A	64
COOH	NiCl.	101		Fo(CO)	121
		101		re(CO)3	121

Table 1 ADOMATICITY OF CYCLODUTADIENE DING IN [7 C]L COMDLEVES

\*\* discontinuous conjugation

alternant" structure (including two or more adjacent "single" bonds).

According to the computed aromaticity from table the substituents Z = -CO-R ( $\hat{R} = H, CH_{a}, OH, OCH_{a}$ ) increase the aromaticity more than Z = -O-R (R = H,  $CH_2$ , Ph) substituents. The ligands  $L = PdCl_{2}$  and  $L = Fe(CO)_{3}$ increase the aromaticity more than other analyzed ligands. The influence of the  $Mo(CO)_4$  ligand is ambiguous. The complexes where Z = H;  $L = Mo(CO)_{4}$  and Z = COOH; L

complexes where Z = H;  $L = MO(CO)_4$  and Z = COOH;  $L = PdCl_2$  present the largest computed aromaticity of a cyclobutadiene ring. If Z = OH the cyclobutadiene ring presents two or more adjacent "single" bonds. In the [Z\_C]L complex from table 1 the C – L bonds are computed as "coordinative" or "single". If Z = H,  $CH_3$ ,  $C(CH_3)_3$ ,  $Si(CH_3)_3$ , Ph and  $L = NiCl_2$ , PtCl\_2 all C – L bonds are computed as "single". If  $L = Fe(CO)_3$  all C – L bonds are computed as "coordinative".

Previously, few authors described some dimers of cyclopentadiene and dihydrofulvene complexes [33, 34]. Here, we analyzed three dimers of  $[Z_{L}C]L$  complexes. These dimers present some features:

-the computed aromaticity of the cyclobutadiene rings seems to be similar or larger than the aromaticity of the cyclobutadiene ring of the monomer from table 1.

 $A \sim 270$  in the dimer of the Z = H, L = PdCl<sub>2</sub> complex

A~ 193 in the dimer of the Z = CH<sub>3</sub>, L = PdCl<sub>2</sub> complex A~ 250 in the dimer of the Z = H, L = Mo(CO)<sub>4</sub><sup>2</sup> complex - the metal - carbon bonds and Pd - Cl bonds are computed as "coordinative" (B  $\sim 0.400$ )

- the Mo – CO bonds are computed as "single" (B  $\sim$ 0.800)

- the monomers in the dimer are bonded by very weak bonds (B < 0.100)

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