Electronic Nature of Planar Cyclobutenyl Dication Derivatives

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The cyclobutadiene dication was not experimentally characterized to the date. However, some of its derivatives were. Most of them have planar geometry, but tetramethylcyclobutadiene dication has a nonplanar geometry according to ab initio calculations. From the atoms in molecules (AIM) theoretical analysis, common electronic features for the planar and puckered cyclobutenyl dication derivatives were observed. The planar cyclobutenyl dication derivatives have bond order of chemical bonds in the ring close to unity and relatively small electronic density in the ring. The puckered cyclobutadiene dication and its puckered derivatives have relatively high electronic density in the ring.

Introduction

Theoretical calculations indicate that cyclobutadiene dication is an aromatic species according to Hückel rules.[1] However, it has never been experimentally characterized. It is probably not subject to Jahn−Teller distortion forces, but considerable charge−charge repulsion arising from the dispersion of two units of charge over only four carbon centers counteract the stabilizing electronic features of this Hückeloid system.[2] On the other hand, some of its derivatives have been successfully synthesized in superacid solution of SbF_5-SO_2 or SbF_5-SO_2ClF at low temperatures (−75 to −65 °C). Olah and co-workers[3] synthesized the tetramethylcyclobutenium dication from 3,4-dichloro-1,2,3,4-tetramethylcyclobutene. The tetraphenylcyclobutadiene dication was also prepared from 3,4-dibromotetraphenylcyclobutene.[4] Olah and Staral[5] obtained 1,2-difluoro-3,4-diphenylcyclobutene dication from 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene, and 1,2-diphenylcyclobutadiene dication from *cis*-3,4-dibromo-1,2-diphenylcyclobutene. Moreover, 1,2-dimethylbenzocyclobutadiene dication involving six- and four-membered rings fused in a 6π aromatic system is a stable and characterized species.[6]

Schleyer and co-workers[7] verified by ab initio calculations that tetramethylcyclobutadiene dication has a nonplanar geometry while tetrafluorcyclobutadiene dication has a planar geometry. They have shown that D_{4h} cyclobutadiene dication is a transition structure for the folded D_{2d} minimum.[8] The D_{2d} symmetry of tetramethylcyclobutadiene dication is similar to the D_{2d} cyclobutadiene dication. The charge in the former is greatly stabilized by methyl groups relative to the latter.[8] The D_{2d} tetra-*tert*-butylcyclobutadiene dication is extremely unstable, as shown in ab initio calculations.[8] In order to better understand the cyclobutadiene dication and its derivatives, these systems were studied from the atoms in molecules theory (AIM) point of view.

Computational Methods

Geometry optimization, vibrational analysis, and the generation of the electronic density were obtained with Gaussian 03.[9] The geometries were optimized on the DFT level by employing the Becke three-parameter interchange functional[10] (B3) in conjunction with the Lee−Yang−Parr[11] correlation functional (LYP) and the split valence basis set[12] 6-311++G**. All geometries were characterized as stationary points after vibrational analysis. The AIM 2000 software[13] was used for charge density calculations from the electronic densities (ρ) obtained at the B3LYP/6-311++G** level. The use of Kohn−Sham orbitals for the calculation of delocalization indices is a good approximation, although not strictly correct.

Results and Discussion

All studied systems are shown in Scheme 1. They were analyzed by AIM theory, which is based on the analysis of the electronic density distribution, $\rho(r)$, obtained from a quantum mechanical wavefunction.[14] Although DFT does not generate a wave function, it yields a density matrix similar to that from a post-HF method such as MP2. Much information can be obtained from AIM, such as the bond, cage, and ring critical points and their respective eigenvalues (see the Supporting Information).

The geometry optimization of all studied dications leads to planar structures only in the cases of the dications **7**, **8**, **10**, and **11**. In spite of having $4n + 2$ π-electrons (where $n = 0$), cyclobutadiene dication is not planar.[15,16] The alkyl derivatives of the cyclobutadiene dication **2**−**6** and the lithium-substituted one, **9**, also have puckered structures. On the other hand, the tetramethylcyclobutenium dication (**5**) is planar, as shown by NMR in superacid media at low temperatures.[3] Probably, the solute−solvent interaction induces **5** to adopt planar structure in solution media.

An important parameter used in this work is the delocalization index (DI). It is important to highlight that the delocalization index does not measure the delocalization of valence electrons over the whole molecular system. Indeed, it is a measure of the number of electrons that are shared or exchanged between two atomic basins from integration of the Fermi hole density.[17] Although DFT does not yield a pair density matrix, the delocalization indexes from B3LYP are close to those from MP2 (see the Supporting Information).

The delocalization index can also be used to estimate the bond order of a covalent bond. The DI does not measure the bond

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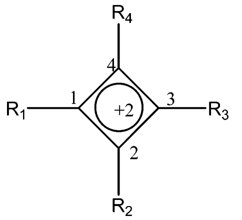
SCHEME 1



1, $R_1= R_2= R_3= R_4=$ H
2, $R_1=CH_3$; $R_2= R_3= R_4=$ H
3, $R_1= R_2= CH_3$; $R_3= R_4=$ H
4, $R_1= R_2= R_3= CH_3$; $R_4=$H
5, $R_1= R_2= R_3= R_4= CH_3$
6, $R_1=$ cyclopropyl; $R_2= R_3= R_4=$ H
7, $R_1= R_2=$ phenyl; $R_3= R_4=$ H
8, $R_1= R_2= R_3= R_4=$ phenyl
9, $R_1= R_2= R_3 = R_4=$ Li
10, $R_1= R_2= R_3= R_4=$ F
11, $R_1= R_2= R_3= R_4=$CN

TABLE 1: Delocalization Indexes (DI) between Ring Carbon Atoms of Cyclobutenyl Dication and Its Derivatives

	delocalization indexes					
entry	C_1-C_2	C_1-C_4	C_2-C_3	C_3-C_4	C_1-C_3	C_2-C_4
1	1.211	1.210	1.209	1.210	0.358	0.358
2	1.137	1.137	1.276	1.273	0.392	0.254
3	1.186	1.189	1.187	1.186	0.334	0.213
4	1.123	1.126	1.231	1.234	0.321	0.237
5	1.164	1.162	1.162	1.166	0.264	0.264
6	1.079	1.069	1.337	1.322	0.142	0.416
7	1.080	1.080	1.230	1.230	0.283	0.130
8	1.091	1.102	1.084	1.084	0.155	0.155
9	1.308	1.304	1.309	1.301	0.519	0.519
10	1.063	1.063	1.063	1.063	0.235	0.235
11	1.112	1.112	1.112	1.112	0.171	0.171

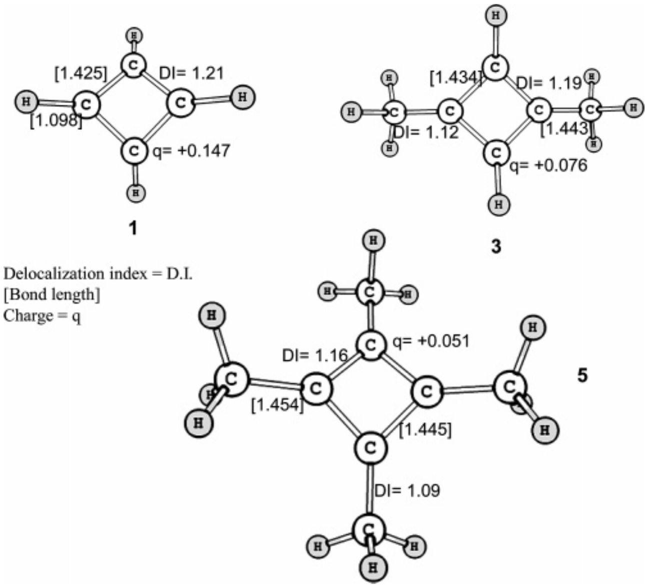


Figure 1. Delocalization indexes, bond lengths (Å), and atomic charges (au) of carbon atoms of the ring in the dications **1**, **3**, and **5**.

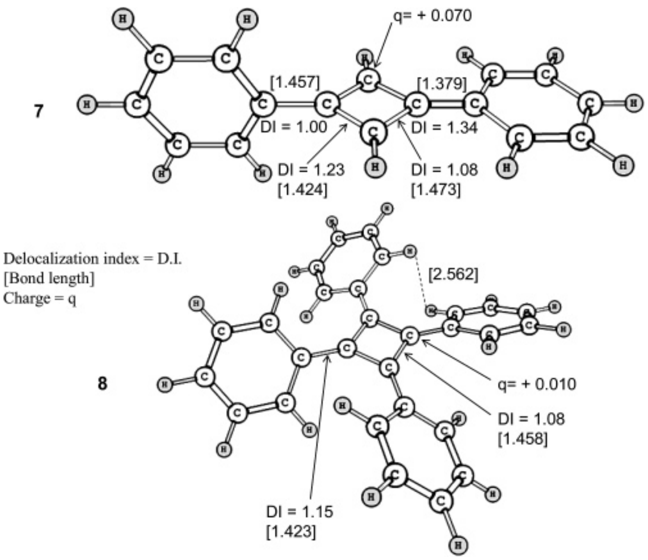


Figure 2. Delocalization indexes, bond lengths (Å), and atomic charges (au) of carbon atoms of the ring in dications **7** and **8**.

order, but they can be directly related. In H_2 molecule, for example, DI = 1.0, which means that one electron is shared between two hydrogen basins. The C−C bond in ethane has DI = 1.0 and the C═C bond in ethylene has DI = 1.9. In benzene, the DI between carbon atoms is 1.30. In hexatriene, the DIs are 1.74 (for double bond) and 1.14 (for single bond). These values are directly related to their bond orders (see the Supporting Information).

One can see from Table 1 that delocalization indexes between vicinal carbon atoms of the ring (C_1-C_2, C_1-C_4, C_2-C_3, and C_3-C_4) in alkyl-substituted dications **1**−**5** and lithium-substituted **9** are higher than 1. They are larger in the dications **1** and **9**. This means that all the chemical bonds involving the carbon atoms in their rings are not single C−C bonds. The cyclopropyl-substituted dication **6** and phenyl-substituted **7** also have two chemical bonds in the ring with DI higher than 1. The dications **1**−**5** and **9** also have the highest delocalization indexes between nonvicinal carbon atoms of the ring (C_1-C_3 and C_2-C_4). This is indicative that they have higher electron density in the ring than other dications.

Figure 1 shows delocalization indexes and bond lengths involving carbon atoms in the ring of the dications **1**, **3**, and **5** along with their respective atomic charges. As mentioned before, none of these dications have planar rings. The folded geometry of the dication **5** was also verified by Schleyer and co-workers.[7,8] The atomic charge was also calculated by the AIM method. The positive charges in the carbon atoms of the ring are higher in the dication **1** and smaller in the dication **5**. The dication **3** has intermediate values of positive charges in the carbon atoms of the ring. Figure 2 depicts the diphenyl-substituted dication **7** and tetraphenyl-substituted dication **8**, which have planar rings. Positive charges in the carbon atoms of their rings are smaller than those from the tetramethyl-substituted dication **5**. Unlike the dications **1**−**6**, the delocalization indexes between carbon atoms in the ring of the dication **8** are close to 1, which means that these C−C chemical bonds are approximately single ones.

Figure 3 depicts the molecular graph of the dications **9**−**11**. The molecular graph is obtained from the AIM method and shows all ring and bond critical points. The positive charges in carbon atoms of the ring of fluorine-substituted dication **10** are higher than those from the dication **1**. However, it has a planar ring. Furthermore, Olah and Staral[5] obtained 1,2-difluoro-3,4-diphenylcyclobutene dication, and this reinforces the stabilizing role of fluorine atom in the dication cyclobutadiene system. In the dications **10** and **11**, the delocalization indexes involving the carbon atoms of their rings are close to 1, indicative of single C−C bonds in the ring. The dication **9** has no planar ring and the delocalization indexes involving the carbon atoms of its ring are nearly the same as those from benzene. Furthermore, the atomic charges of the carbon atoms of its ring have considerable negative values.

Table 2 shows the mean delocalization index among vicinal and nonvicinal carbon atoms of the ring, vicinal and nonvicinal $\overline{\text{DI}}$, respectively, along with the electron density of the ring critical point, average charge of carbon atoms of the ring, and dihedral angle involving these atoms (ring dihedral angle). The mean delocalization index among nonvicinal carbon atoms of the ring and the electron density of the ring critical point are indicative of the electron density inside the ring. The dications

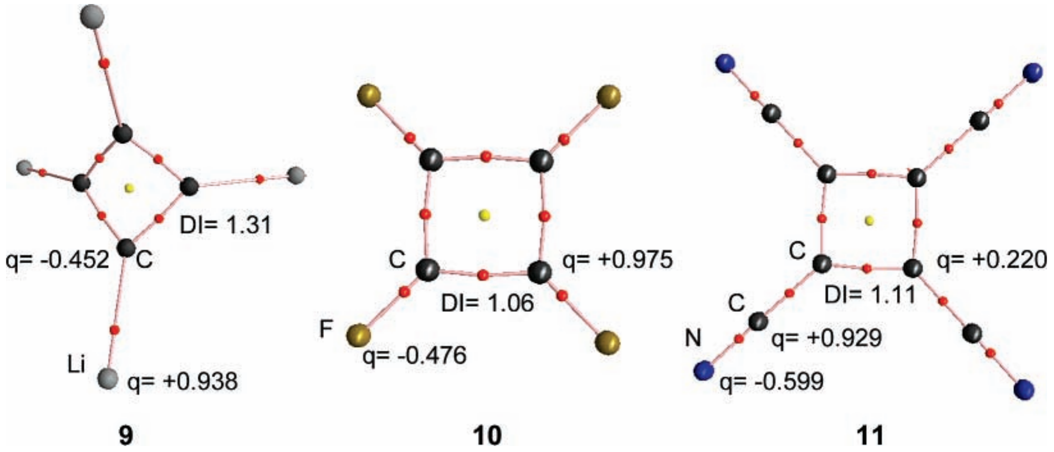


Figure 3. Molecular graph of dications **9**−**11** and the delocalization indexes and atomic charges of their carbon atoms of the ring.

TABLE 2: Dihedral Angles Involving Carbon Atoms of the Ring (Ring Dihedral Angle), Number of Imaginary Frequencies, Mean Delocalization Index of Vicinal Carbon Atoms in the Ring (vicinal $\overline{\text{DI}}$), Mean Delocalization Index of Nonvicinal Carbon Atoms in the Ring (nonvicinal $\overline{\text{DI}}$), Ring Critical Point (ρ[3,+1]), and Average Charge of Atomic Basins in the Ring of Cyclobutenyl Dication and Its Derivatives

			$\overline{\text{DI}}$			
entry	ring dihedral angle, deg	no. of imaginary frequencies	vicinal	nonvicinal	ρ[3,+1]	av charge[a] (au)
1	30.5	0	1.210	0.358	0.094	+0.147
2	28.3	0	1.206	0.323	0.123	+0.107
3	28.7	0	1.187	0.273	0.125	+0.075
4	23.6	0	1.178	0.279	0.115	+0.059
5	21.2	0	1.163	0.264	0.112	+0.053
6	22.4	0	1.202	0.279	0.120	+0.070
7	0	2	1.155	0.206	0.105	+0.008
8	0	0	1.090	0.155	0.101	+0.011
9	41.7	0	1.305	0.519	0.142	-0.452
10	0	0	1.063	0.235	0.092	+0.968
11	0	0	1.112	0.171	0.054	+0.220

[a] Average charge of atomic basins in the ring of cyclobutenyl dication and its derivatives.

with nonplanar rings have nonvicinal $\overline{\text{DI}}$ higher than 0.264, and those with planar rings have nonvicinal $\overline{\text{DI}}$ ranging from 0.155 to 0.235. All the dications with nonplanar rings have electron density in the ring critical point higher than 0.112, except for the dication **1**. Then one can observe that the dications with nonplanar rings have higher electron density in the ring than those with planar rings. Moreover, dications with a nonplanar ring have vicinal $\overline{\text{DI}}$ higher than 1.163, while in the dications with a planar ring it ranges from 1.063 to 1.155. Then, in the dications with a nonplanar ring, bond orders of C−C chemical bonds in the ring are higher than 1, while they are close to 1 in dications with a planar ring, except for the dication **7**.

In all dications with no heteroatom substituents (**1**−**8**) there exists a direct relation between ring dihedral angle and average atomic charge of carbon atoms in the ring (Table 2). Within those with a nonplanar ring, the dication **1** has the highest ring dihedral angle and average positive charge of atoms in the ring and the dication **5** has the smallest ones. The dications **7** and **8**, with a ring dihedral angle of 0°, have the smallest average charge of atoms in the ring.

In a previous work it was shown that cyclobutadiene and cyclooctatetraenyl dianions have planar structures while their corresponding dication parents have puckered structures.[18] For cyclobutadiene and cyclooctatetraenyl dianions, it was concluded that their corresponding 6π-electron resonance and 10π-electron resonance compensate the Coulombic repulsive interaction. The 2π-electron resonance in the cyclobutadiene dication and the 6π-electron resonance in an eight-membered ring of cyclooctatetraenyl dication do not compensate their Coulombic repulsion and they adopt a puckered structure. Then, as repulsive Coulombic forces decrease from the dication **1** to **8**, the ring tends to be more planar.

On the other hand, the dication **9**, with a nonplanar ring, has an average negative charge of atoms in the ring, while the dication **10**, with a planar ring, has the highest positive charge of atoms in the ring. Olah and Staral[5] assumed that fluorine atoms back-donate its nonbonded electrons to the cyclobutadiene dication ring in 1,2-difluoro-3,4-diphenylcyclobutene dication. However, in the fluorine-substituted dication **10**, this does not happen, because of the small electron density in its ring and its negatively charged fluorine atoms (Table 2). In this case, the π-electron system interacts with fluorine atoms.

Olah and co-workers[3,5] obtained the tetramethylcyclobutenium dication (**5**) experimentally, and its cyclobutadiene moiety has planar geometry. Its electronic nature, as shown in Table 2, is close to those that have a planar butadiene dication ring and no heteroatoms (dications **7** and **8**). The planar structure of the dication **5** in solution media is probably due to the ability of the solvent molecules to delocalize the electronic charge in the ring of **5**, since planar cyclobutadiene dication derivatives have relative small electronic density in the ring.

Three electronic parameters are common for dications with planar rings and no heteroatom substituents: (1) low positive charge in the ring atoms, (2) a bond order of C−C chemical bonds in the ring close to 1, and (3) a relatively small electron density in the ring. For dications with heteroatom substituents, only the last two parameters are valid.

One can observe that the four-membered ring is planar when the heteroatom substituents are electronegative or when nonheteroatom substituents have the ability to delocalize the positive charge and electron density along them.

Conclusion

Two electronic features are characteristic for cyclobutenyl dication derivatives with a planar ring: the bond order of chemical bonds in the ring close to 1 and relatively small electronic density in the ring. One electronic feature is common for puckered cyclobutadiene dication and its puckered derivatives: high electronic density in the ring.

Cyclobutadiene dication derivatives are planar when the heteroatom substituents are electron-withdrawing or when nonheteroatom substituents have the ability to delocalize the positive charge and electron density along them. On the other hand, cyclobutadiene dication and methyl- and cyclopropyl-substituted dications **2−6** have puckered geometry because they have higher positive charge in the carbon atoms of the ring and higher electronic density in the ring. The puckered lithium-substituted **9** has also high electronic density in the ring.

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Supporting Information Available: Atoms in molecules (AIM) theory, bond order and delocalization index, comparison of delocalization indexes between MP2 and B3LYP, computed energy values of species **1−11**, and **Z** matrices of optimized structures. Total energies and geometry coordinates are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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