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The [2+2] Cycloaddition Product of Perhalogenated Cyclopentadienyl Cations: Structural Characterization of Salts of the [C₁₀Cl₁₀]²⁺ and [C₁₀Br₁₀]²⁺ Dications

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Instead of monomeric cyclopentadienyl cations, the low-temperature reaction of hexachloro- and hexabromocyclopentadiene (C_5Cl_6 and C_5Br_6) with powerful Lewis acids SbF_5 and AsF_5 in SO_2ClF yields salts of perhalogenated dications [$C_{10}Cl_{10}$][Sb_3F_{16}]₂ and [$C_{10}Br_{10}$][As_2F_{11}]₂ which are characterized via single crystal X-ray diffraction and NMR spectroscopy. Additionally, this reactivity is rationalized by quantum-chemical calculations.

Carbocations have been an equally important and fascinating research field in organic chemistry for many decades.¹ But even lately, important landmarks have been reported, e.g. the structural characterization of the 2-norbornyl cation and of the pentagonal pyramidal hexamethylbenzene dication with a hexacoordinated carbon atom.^{2, 3} One important carbocation that so far has resisted all attempts at isolation and crystallization due to its instability, is the cyclopentadienyl cation. As the cyclopentadienyl cation has an antiaromatic $4-\pi$ electron system the ground state of [C₅H₅]⁺ is a (diradical) triplet state.⁴ This is also the case for $[C_5(^{i}Pr)_5]^{+5}$ and $[C_5Cl_5]^{+6}$, while for [C₅Ph₅]⁺ a singlet ground state seems to be favored although in general the singlet-triplet energy gap is usually very small in these systems.^{6, 7} While $[C_5H_5]^+$ dimerizes,⁸ the pentaphenyl cyclopentadienyl cation decomposes via C-H cleavage and formation of additional C-C bonds - some of the decomposition products have been identified.9 Although permethylation is an effective strategy to stabilize highly electrophilic cations^{3, 10-13} this is not the case for the cyclopentadienyl cation. Jutzi reported that [C₅Me₅]⁺ decomposes via loss of a proton and polymerization subsequent of the resulting tetramethylfulvene.¹⁴ Surprisingly, in 2002 the structural characterization of the stable [C₅Me₅]⁺ cation was reported but this result turned out to be erroneous.¹⁵ The reduced species that had been isolated instead, turned out to be $[C_5Me_5H_2]^+$,¹⁶⁻¹⁹ being a rare example of an allylic cation without stabilizing heteroatoms or additional π -systems.²⁰⁻²² Hydrogenabstraction from the organic solvent also seems to cause the decomposition of $[C_5(i-Pr)_5]^{+.5}$

In order to block decomposition pathways via the hydrogen atoms, the synthetic target of a perhalogenated cyclopentadienyl cation is very appealing.²³ Breslow *et al.* observed the formation of a triplet state cyclopentadienyl cation after reaction of C₅Cl₆ with neat antimony pentafluoride by EPR spectroscopy.^{6, 24} However, the triplet signal of the presumed [C₅Cl₅]⁺ in the SbF₅ matrix vanishes rapidly above the freezing point of SbF₅. Quenching experiments with methanol resulted only in < 5% C₅Cl₅OCH₃ but >90 % dimeric perchlorinated ketones.⁶ This can be explained by the tendency of C₅Cl₆ to either dimerize or polymerize in presence of Lewis acids (e.g. AlCl₃).²⁵⁻²⁷

For this study, we decided to (re-)investigate the reaction of C_5Cl_6 and C_5Br_6 with the powerful Lewis acids SbF_5 and AsF_5 in the non-coordinating solvent SO_2ClF at low temperatures (Scheme 1). Single crystals of compounds $[C_{10}Cl_{10}][Sb_3F_{16}]_2 \cdot SO_2ClF$ (4a) and $[C_{10}Br_{10}][As_2F_{11}]_2 \cdot 2 SO_2ClF$ (4b) were obtained from the reaction mixtures at -75 °C. The compound 4a crystallizes in monoclinic space group $P2_1/n$ and 4b in triclinic space group $P\overline{1}$. The asymmetric units contain a $[C_5X_5]$ unit as well as one monoanion, respectively (Figure 1). Due to a center of inversion the overall formula are $[C_{10}Cl_{10}][Sb_3F_{16}]_2$ and $[C_{10}Br_{10}][As_2F_{11}]_2$. Based on the variations





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in C-C bond lengths, the bonding situation in these dications is best described as two allyl cations separated by a saturated four-membered ring (see SI, Table S3).



Figure 1: Ellipsoid (50% probability at 100 K) plot of compounds [C₁₀Cl₁₀][Sb₃F₁₆]₂ • SO₂ClF (left; 4a) and [C₁₀Br₁₀][As₂F₁₁]₂ • 2 SO₂ClF (right, 4b). Counterions and solvent molecules are omitted for clarity. Color code: red – bromine, green – chlorine, grey – carbon.

Interestingly, the C-Cl bond lengths vary considerably within the dication. In comparison with the C-Cl bond lengths in C₅Cl₆ (C_{sp3}-Cl: 1.780(2)-1.781(2) Å; C_{sp2}-Cl: 1.696(1)-1.699(2) Å) the C-Cl bonds C1-Cl1 and C5-Cl5 from the saturated fourmembered ring in **4a** are slightly shortened (1.739(2)-1.740(2) Å). However, the so-called α -chlorine effect is even more evident in the allyl cation: Here, the C2-Cl2 and C4-Cl4 bonds are shortened to 1.643(2) and 1.634(2) Å while the effect is less pronounced for C3-Cl3 (1.678(2) Å). This finding is in accordance with calculated NBO charges (see SI) which are the highest for Cl2 and Cl4. In general, the high electrophilicity of the allyl cation is reduced by chlorine as a π -donor (+M-effect). The same effects can be observed for the perbrominated dication **4b** (Table 1). The resulting bond-shortening of the C-halogen bond in carbocations has been observed before.²⁸⁻³⁴

Table 1: Selected bond lengths of the compounds 1a, 1b, 4a and 4b in [Å].

	C ₁₀ X ₁₀ ²⁺ (X=CI) 4a	C ₁₀ X ₁₀ ²⁺ (X=Br) 4b
C1-X1	1.740(2)	1.908(4)
C2-X2	1.643(2)	1.803(6)
C3-X3	1.678(2)	1.833(5)
C4-X4	1.634(2)	1.797(4)
C5-X5	1.739(2)	1.912(5)
	C ₅ X ₆ (X=Cl) 1a	C ₅ X ₆ (X=Br) 1b
C _{sp3} -X	1.780(2)-1.781(2)	1.950(6)
C _{sp2} -X	1.696(1)-1.699(2)	1.838(11)-1.875(11)

Only few examples of crystal structures containing $[Sb_3F_{16}]^-$ ions are known, in which it can exist as either cis or trans isomer.³⁴⁻³⁸ In **4a** the SbF₅ groups are attached to neighbouring *cis*fluorine atoms of a central $[SbF_6]^-$ unit. The number of structures containing $[As_2F_{11}]^-$ is similarly scarce.^{3, 12, 29, 34, 39-43} The structures of **4a** and **4b** show only weak contacts between anion $[Sb_3F_{16}]^-$ and $[As_2F_{11}]^-$ to the allylic carbon centres. The present C···F contact distances of 3.031 and 3.110 Å in the **4a** and 3.096 and 3.158 Å in the **4b** structure are comparable to those observed in $[CCl_3]^+$ ¹⁷ (2.962(9) Å), $[CBr_3]^+$ ¹⁷ (3.09(2) Å), $[C_6Cl_6]^+$ ¹⁹ (3.003(1) Å) and $[C_6Br_6]^+$ (2.994(1) Å).³⁴ The chlorine and bromine atoms also interact with the fluorine atoms of the anion as well as the oxygen atoms of the SO₂CIF molecules (CI· •• F: 2.843 to 3.212 Å; Br ••• F: 2.877 to 3.310 Å; Glicle Online 3.268 Å, Br•••O: 2.975 and 3.196 Å). DOI: 10.1039/D0CC04226A

¹³C and ¹⁹F NMR spectra of **4a** and **4b** were recorded in liquid SO₂ at -60°C while the spectra of 1a and 1b were measured in organic solvents at room temperature. The difference in ¹³C chemical shifts between 1a and 1b, as well as 4a and 4b is most pronounced for the sp³ hybridized carbon atoms. The ¹³C NMR spectra of 4a and 4b display three signals, respectively (see SI) which is consistent with the symmetry of the compounds. The most downfield shifted chemical shifts (4a: 218.08, 4b: 219.32 ppm) correspond to the carbon atoms C2 and C4 which are mostly affected by the positive charges. These signals are significantly deshielded compared to the starting materials (1a: 131.49, 1b: 130.21 ppm) which confirms carbocation formation.⁴⁴ The inner carbon of the allyl cation (C3) resonates at 158.23/155.23 ppm (4a/4b). The four-membered saturated ring is characterized by one signal at 76.05/66.27 ppm (4a/4b). Very similar chemical shifts are observed for [C₁₀(cyclopropyl)₁₀]²⁺ and the lesssymmetric [C₁₀H₈Me₂]²⁺ which both have not been structurally characterized so far.45, 46 The 13C NMR spectrum of the former displays three signals at δ = 222.6 , 148.3 and 83.2 ppm. The ¹⁹F NMR spectrum of 4a (see SI) shows five signals consistent with the counter ion [Sb₃F₁₆]⁻. The ¹⁹F NMR spectrum of **4b** only shows a broad singlet for [As₂F₁₁]⁻ due to fast exchange processes.^{47, 48}



Figure 2: ¹³C NMR chemical shifts of compounds (1) and (4) in [ppm]. $C_{10}CI_{10}^{2+}$ and $C_{10}Br_{10}^{2+}$: 100 MHz, SO₂, ext. acetone-d₆, -60 °C. C₅CI₆: 100 MHz, CH₂CI₂, ext. acetone-d₆, room temperature. C₅Br₆: 100 MHz, CDCI₃, room temperature

The isolation of the $[C_{10}X_{10}]^{2+}$ dications instead of $[C_5X_5]^+$ poses the question how energetically favorable this dimerization is. Although dimerization of the 4π -electron systems and diradicals $[C_5X_5]^+$ appears reasonable, Coulomb-repulsion should destabilize the dication. Structure optimizations and frequency calculations were performed on the B3LYP-GD3BJ/def2-TZVP and MP2/cc-PVTZ level of theory. The optimized structures are in accordance with the crystal structures and the variations in C-C and C-X bond lengths are well reproduced. As expected, the shortest C-X bond lengths are those where the halogen atom (X) carries the highest positive charge (see SI). Calculation of Gibbs free energies for the dimerization of (triplet) $[C_5Cl_5]^+$ (2a) to $[C_{10}Cl_{10}]^{2+}$ and its isomers (4a, 5a and 5b) were performed for a temperature of 213.15 K. While the dimerization of 2a to 4a is endergonic by 225 kJ/mol (using B3LYP-GD3BJ/def2-TZVP), formation of the [4+2] Diels-Alder-products 5a and 5b is even

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less favorable (317/316 kJ/mol). However, these values contradict common chemical experience, especially since the dimerization already takes place at very low temperatures. It is important to note that these calculated values refer to isolated molecules in vacuum. In order to obtain a better description for the experimental parameters, the calculations were repeated with a solvation model, using dielectric constants (relative permittivity) of ϵ_r = 2 and ϵ_r = 10 to simulate the influence of solvents of very low or medium polarity. Additionally, $\varepsilon_r = 23$ was used to model the dielectric constant of liquid SO₂ at 213.15 K.⁴⁹ Taking solvation into account the dications become significantly more stable, reducing the overall Gibbs free energy of the formation of $[C_{10}CI_{10}]^{2+}$ (4a) to +108, +35 and +5 kJ/mol, respectively (for ε_r = 2; 10; 23). The Diels-Alder-products *exo*-5a and endo-5a remain about 100 kJ/mol less stable than 4a. If MP2/cc-PVTZ instead of DFT is used for the calculations, all Gibbs free energies are roughly shifted by 100-150 kJ/mol in favor of the dications. Consequently, dimerization is slightly favorable even for extremely non-polar solvents ($\varepsilon_r = 2$) but becomes significantly exergonic for 4a and **5a** in medium-polar solvents ($\varepsilon_r = 10$ and 23). For $[C_{10}Br_{10}]^{2+}$ the general trend is clearly the same for the DFT calculations, although the calculations using MP2/cc-PVTZ were not performed for $[C_{10}Br_{10}]^{2+}$ due to the enormous demand of computational resources (see SI).



Figure 3: Top: perhalogenated cyclopentadiene derivatives (1) as well as triplet state (2) and singlet state (3) cyclopentadienyl cations. Bottom: [2+2] cycloaddition product (4) and [2+4] cycloaddition products of two cyclopentadienyl cations.

Dutton proposed a series of possible substitution patterns (typically, CH₃, CF₃, C₆H₅, C₆F₅ substituents) which could give rise to a stable cyclopentadienyl cation.⁵⁰ Possible side-reactions (proton loss, addition of fluoride etc.) were taken into account. By using M06-2X/def2-TZVP, B3LYP/def2-TZVP and the polarizable continuum model to account for solvent effects of dichloromethane ($\varepsilon_r \approx 9$), he calculated that the dimerization to dicationic (*exo/endo*)-Diels-Alder-products similar to **5a** is endergonic by about 195-212 kJ/mol which is similar to our calculations. Since we can experimentally prove that dimerization occurs (however to products that are even about 50-100 kJ/mol more stable), we have to assume that the probability is low to achieve a stable, monomeric cyclopentadienyl cation with this approach. Even worse, also lattice energies work

against isolation of the monomeric cation in the solid state, the control of the monomeric cation in the solid state, the control of the monomeric cation in the solid state, the control of the A⁺ X⁻ salt has a significantly lower lattice energy than a the solid state, the control of the dimerization. The gain of the higher lattice energy could lead to the isolation of the dimerization products. Only for extremely large weakly-coordinating anions the energy differences between these different stoichiometries would become relatively small and could in principal be overcome by a highly endergonic dimerization. However, the numbers of our MP2 calculations suggest that this is definitely not the case here.

Table 2: Calculated energy differences ΔG in kJ/mol at 213.15 K. ε_r is the dielectric constant, used for calculations with the Polarizable Continuum Model (PCM) for solvent effects.

	B3LYP-GD3BJ/def2-	MP2/cc-pVTZ
	TZVP	
2a / 3a	0 / +32	0/ +15
2a + 2a → 4a / exo-	+225/+317/+316	+102/+156/+165
5a / endo-5a		
2a + 2a → 4a / exo-	+108/+195/+201	-13/+37/+41
5a / endo-5a ; ϵ_r =2		
2a + 2a → 4a / exo-	+35/+103/+101	-109/-61/-61
5a / endo-5a ; ϵ_r =10		
2a + 2a → 4a / exo-	+5/+89/+90	-123/-75/-76
5a / endo-5a ; ϵ_r =23		

These results suggest that in order to isolate a monomeric cyclopentadienyl cation the most promising strategy is to design sterically bulky Cp rings, where sterics destabilize the dication. Additionally, the larger molecular volume of the cation also beneficially reduces the lattice energies. However, as stated in the introduction, this is very difficult from a synthetic point of view since C-H containing systems seem to be very prone to all sorts of decomposition reactions.

In summary, $[C_{10}CI_{10}][Sb_3F_{16}]_2$ and $[C_{10}Br_{10}][As_2F_{11}]_2$ are the first structurally characterized dications which are derived from the dimerization of a substituted cyclopentadienyl cation. To our knowledge, only one perhalogenated dication had been structurally characterized so far $([C_{14}F_{10}]^{2+})$.⁴² The bonding situation in $C_{10}X_{10}^{2+}$ is best described as two allyl cations that are separated by a fourmembered saturated ring. The chlorine and bromine atoms act as efficient π -donors into the allyl-cation, which is reflected by significant shortening of C-Cl and C-Br bonds.

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Conflicts of interest

There are no conflicts to declare.

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The [2+2] Cycloaddition Product of Perhalogenated Cyclopentadienyl Cations: Structural $\frac{View Article Online}{DOI: 10.1039/D0CC04226A}$ Characterization of Salts of the $[C_{10}Cl_{10}]^{2+}$ and $[C_{10}Br_{10}]^{2+}$ Dications

Susanne Margot Rupf, Patrick Pröhm and Moritz Malischewski

Perchlorinated and perbrominated organic dications $[C_{10}CI_{10}]^{2+}$ and $[C_{10}Br_{10}]^{2+}$ have been obtained instead of monomeric cyclopentadienyl cations $C_5CI_5^+$ and $C_5Br_5^+$.

