JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by UNIVERSITY OF ADELAIDE LIBRARIES

Article

Isolation of an Antiaromatic Singlet Cyclopentadienyl Zwitterion

Paolo Costa, Iris Trosien, Joel Mieres-Pérez, and Wolfram Sander

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b05807 • Publication Date (Web): 22 Aug 2017

Downloaded from http://pubs.acs.org on August 22, 2017

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Isolation of an Antiaromatic Singlet Cyclopentadienyl Zwitterion

Paolo Costa, Iris Trosien, Joel Mieres-Perez, and Wolfram Sander*

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Supporting Information Placeholder

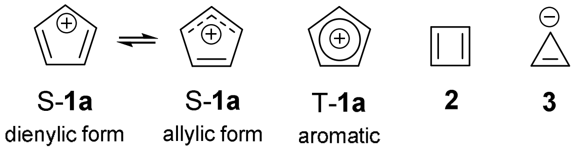
ABSTRACT: The reaction of triplet tetrachlorocyclopentadienylidene with BF$_3$ in rare gas matrices yields a zwitterion consisting of a cyclopentadienyl cation bearing the positive charge and a negatively charged BF$_3$ unit. IR and UV-vis spectra as well as the absence of EPR signals demonstrate a singlet ground state of the zwitterion, and its calculated geometry and magnetic properties clearly reveal a strong antiaromatic character. The zwitterion is highly labile, and by visible or IR irradiation rearranges via a 1,2-fluorine migration from boron to carbon. Interaction with a second molecule of BF$_3$ stabilizes the zwitterion and suppresses the fluorine migration, thus providing a convenient and efficient synthesis of an antiaromatic molecule under very mild conditions.

Introduction

Ever since the term „antiaromaticity“ was introduced by Breslow in the 1960s to describe the destabilization of cyclic conjugated systems containing 4n πelectrons,[1-2] this concept was subject to intense debates.[3] While antiaromaticity became an essential tool for teaching organic chemistry, it is difficult to quantify and escapes rigorous definitions. Therefore, archetypical antiaromatic molecules are essential for the conceptual understanding of antiaromaticity. Since in antiaromatic molecules the cyclic π-conjugation is destabilizing, antiaromatic molecules suffer from distortion to escape this destabilization at least partially. Thus, antiaromatic molecules are transition states, and isolable molecules retain their antiaromaticity only partially.

The cyclopentadienyl cation **1a**, cyclobutadiene **2**, and the cyclopropenyl anion **3** are regarded as iconic 4π-electron (Hückel) antiaromatic molecules (Chart 1).[4] However, as Schleyer et al. noted in 2012, the high energy of **2** is not due primarily to antiaromaticity, but rather to angle strain, torsional strain, and Pauli repulsion between the parallel CC bonds.[5] These authors conclude that “instead of the conventional interpretation of cyclobutadiene as the antiaromatic paradigm, it should be regarded as a unique molecule”. The cyclopropenyl anion **3** was studied in detail by Kass in 2013, and from a correlation between cycloalkene acidities and allylic bond angles, he concludes that **3** is nonaromatic, despite 50 years of belief that it is antiaromatic.[6]

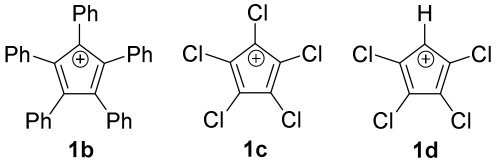
Chart 1. Representative structures of antiaromatic molecules.[a]



[a] S-**1a** and T-**1a** refer to the singlet and triplet states of the cyclopentadienyl cation **1a**, respectively.

This leaves us with the cyclopentadienyl cation **1a** in its singlet state S-**1a** and its derivatives as the prototypical antiaromatic molecules. Breslow et al. studied the pentaphenylcyclopentadienyl cation **1b** (Chart 2) in frozen CH$_2$Cl$_2$ at 77 K by EPR spectroscopy and were able to detect its triplet state T-**1b** by EPR spectroscopy.[7] Although the singlet state could not be directly observed, they conclude that singlet is ground state, but the triplet state lies nearby (less than 1 kcal/mol higher in energy) and is populated even at 77 K.[8]

Chart 2. Representatives structures of cyclopentadienyl cations.



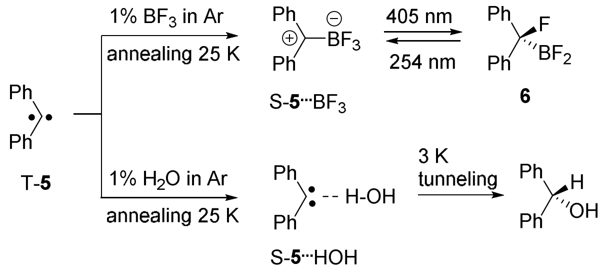
The triplet ground state of the pentachlorocyclopentadienyl cation **1c** in SbF$_5$ matrix was characterized by EPR spectroscopy,[9] and later by IR spectroscopy.[10] The parent cyclopentadienyl cation **1a** was also synthesized in solid SbF$_5$, and EPR spectroscopy revealed its triplet ground state.[11] For both **1a** and **1c** the EPR spectra suggest D_{5h} symmetrical structures. According to Baird’s rule, “*the lowest triplet state for 4n rings is aromatic since the bonding energy is significantly greater than for the diradical reference structure.*”[12-13] Thus, the ground states of **1a** and **1c** have to be considered being aromatic and not antiaromatic. For **1a**, the highly symmetrical triplet ground state $^3A_2'$ was later confirmed by PFI-ZEKE photoelectron spectroscopy.[14-15] The first singlet state of **1a** shows $^1E_2'$ symmetry with strong pseudo Jahn-Teller distortion by interaction with the next higher singlet state, and the singlet-triplet splitting was determined to 1534±6 cm^{-1}

(4.39±0.02 kcal/mol). Interestingly, IR spectra indicate a singlet ground state for the tetrachlorocyclopentadienyl cation **1d** in solid SbF_5.[16] The electronic structure of **1a** and its derivatives have been subject to calculations at various levels of theory.[17-22] These calculations reveal that two Jahn-Teller distorted singlet states show almost identical energies: one is represented best as an allylic state, the other as localized cyclopentadienyl cation (Chart 1). The symmetrical triplet state is close in energy, and depending on substituents triplet or singlet states are slightly preferred, balancing antiaromatic stabilization and electron repulsion.

The synthesis of antiaromatic (singlet) cyclopentadienyl cations is a challenge, mainly due to the lack of suitable precursors and the necessity to use strongly interacting Lewis acids such as SbF_5 as matrix to stabilize the ion pairs. Here, we introduce a new approach for the synthesis of destabilized cations in inert environments: the reaction of carbenes with single molecules of a Lewis acid under the conditions of matrix isolation. Closed shell singlet carbenes are strong Lewis bases, and even if the triplet state of the carbene is ground state, the Lewis acid-base interaction can stabilize the singlet enough to become ground state.[23-28] Thus, hydrogen bonding with water or methanol stabilizes the closed-shell singlet state of diphenylcarbene S-**5** by 9 – 11 kcal/mol and halogen bonding with ICF_3 by 15 kcal/mol, whereas interaction with BF_3 leads to 40 kcal/mol stabilization.[28] In contrast, the stabilization of the triplet state T-**5** is only 4 – 5 kcal/mol and not correlated with the acidity of the interacting Lewis acid. The resulting Lewis acid – base adduct S-**5**···BF_3 is a zwitterion with a positively charged benzhydryl and a negatively charged BF_3 moiety (Scheme 1). Photochemically, S-**5**···BF_3 reversibly interconverts with the B-F insertion product **6** via migration of a fluorine atom. The UV-vis absorption of the benzhydryl moiety in S-**5**···BF_3 is almost identical to that of the matrix-isolated benzhydryl cation, indicating the positive charge of the benzhydryl unit.

This method provides a new approach for the synthesis of cationic units as part of zwitterions at cryogenic temperatures under the very mild conditions of matrix isolation. It is tempting to apply this method to the synthesis of even less stable cationic units such as the highly destabilized antiaromatic cyclopentadienyl cations with the goal to characterize these species spectroscopically and to study their chemistry.

Scheme 1. Reactions of diphenylcarbene 5 with BF_3 and H_2O.

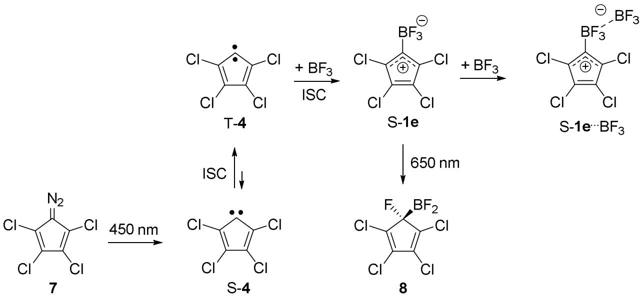


Results and Discussion

Matrix Isolation Experiments. For our studies, we selected tetrachlorocyclopentadienylidene **4**, a well-studied triplet ground state carbene[29] which is easily prepared by 450 nm photolysis of matrix-isolated diazo compound **7** at 3 K. In initial experiments, we investigated the reaction of T-**4** with isolated water molecules in 1% H_2O-doped argon matrices. At temperatures below 10 K, argon matrices are very rigid, and the diffusion of water molecules is completely suppressed. To allow diffusion, and thus bimolecular reactions, the matrix was slowly warmed from 3 K to 25 K. In similar experiments, triplet diphenylcarbene T-**5** is converted to a strongly hydrogen bonded complex of singlet carbene S-**5** with water (Scheme 1).[24] In contrast, T-**4** forms only weakly bound complexes with H_2O, and spin inversion to S-**4** is not observed (Figure S1). The stabilization of S-**4** by hydrogen bonding is thus not large enough to overcome the S-T splitting in **4**. This might be caused by either a larger S-T gap in **4** compared to that in **5** or by a weaker stabilizing interaction of S-**4** with water compared to S-**5**.

The stabilizing interaction of S-**4** with BF_3 is much larger than that with H_2O, and the formation of a singlet adduct can be expected. Upon annealing of an 1% BF_3-doped argon matrix containing T-**4** for 10 minutes to 20 K, the IR bands of BF_3 and T-**4** decrease, and new peaks appear in the spectrum. Besides the formation of oligomers of boron trifluoride, two intense IR bands at 1285.7 cm^{-1} and at 1304.2 cm^{-1} and several weaker IR bands are formed. Further annealing of the same matrix at 25 K and 30 K for 10 minutes each changes the intensity ratio of the two intense peaks in favor of the 1304.2 cm^{-1} band (Figure 1). This clearly indicates that these bands belong to two different species A (1285.7 cm^{-1}) and B (1304.2 cm^{-1}).

Scheme 2. Reactions of tetrachlorocyclopentadienylidene 4 with BF_3.



Compound A is extremely photolabile, and by red light (650 nm) or even IR light (source of the spectrometer) irradiation readily rearranges into a new species C. By comparison with spectra calculated at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory, we assign species A to the Lewis acid – base adduct **1e**, and its photoproduct to the formal B-F insertion product **8** (Scheme 2, Figure 2 and Tables S3 and S5). DFT calculations predict almost degenerate energies of the lowest lying singlet and triplet state of **1e**. The IR spectrum is in excellent agreement with the singlet state S-**1e** and does not indicate the presence of T-**1e**. EPR spectroscopy reveals that **1e** is EPR silent, thus confirming the singlet ground state of **1e**. The UV-vis spectrum of **1e** shows a broad absorption with a maximum at 320 nm, in reasonable agreement with results from TD-DFT calculations (Figure S9).

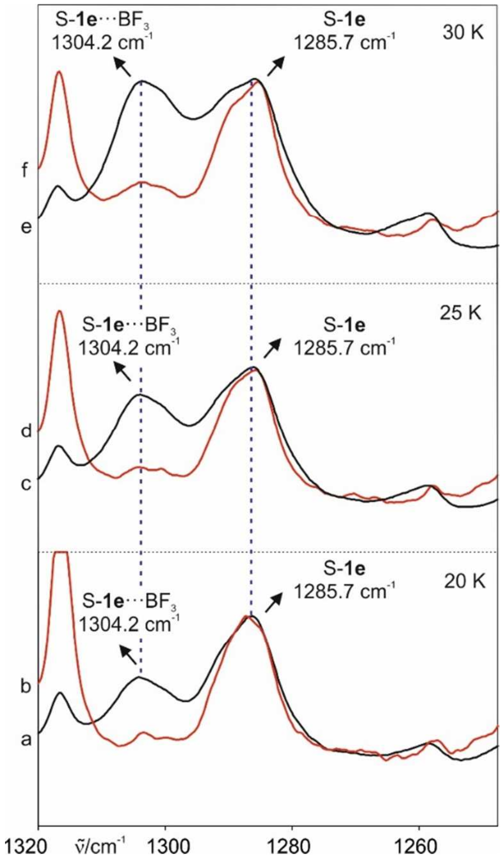


Figure 1. IR spectra showing the effect of annealing of matrices containing carbene T-**4** and either 1% BF$_3$ (black line) or 0.1% BF$_3$ (red line) at temperatures between 20 and 30 K. The C-C-C str. region of the products S-**1e** and S-**1e**···BF$_3$ are shown. a) 20 K, 1% BF$_3$. b) 20 K, 0.1% BF$_3$. c) 25 K, 1% BF$_3$. d) 25 K, 0.1% BF$_3$. e) 30 K, 1% of BF$_3$. f) 30 K, 0.1% BF$_3$.

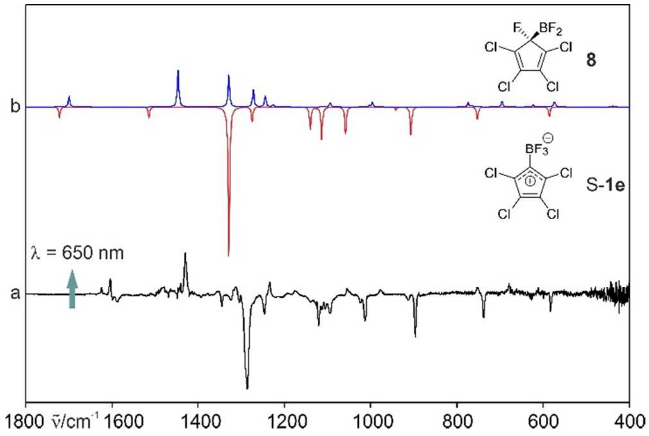


Figure 2. IR spectra showing the photochemistry of S-**1e**. a) Difference IR spectrum showing changes after 650 nm of an argon matrix at 3 K containing **1e**. Bands pointing downwards are assigned to **1e** and bands pointing upwards to **8**. b) Computed IR spectrum of **1e** (multiplied by -1, peaks pointing downwards) and computed IR spectrum of **8** (peaks pointing upwards) at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory.

Compound B is much less sensitive to irradiation, and UV light (365 nm) is required for its photolysis. The yield of B increases at higher annealing temperatures of the matrix (25 – 30 K), longer diffusion times, and with increasing concentrations of BF$_3$ in the matrix (Figure 1). At very low concentrations of BF$_3$ (0.1%), mainly A and only traces of B are formed. This indicates that more than one molecule of BF$_3$ is required for the formation of B, and by comparison with DFT calculations we assign B to S-**1e** interacting with a second molecule of BF$_3$ (Scheme 2, Figure 3 and Figure S3).

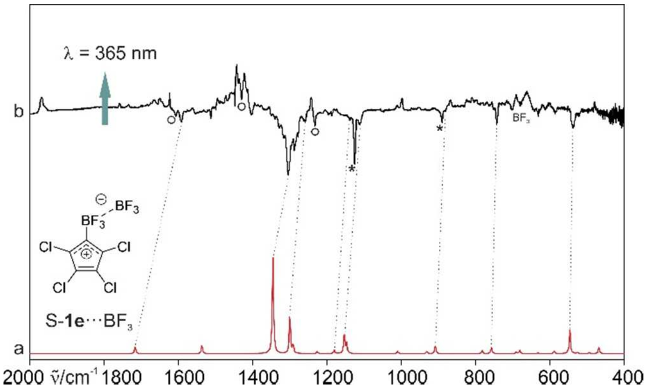


Figure 3. IR spectra showing the photochemistry of S-**1e**···BF$_3$. a) IR spectrum of S-**1e**···BF$_3$ calculated at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory. b) Difference IR spectrum showing changes after 365 nm irradiation an argon matrix at 3 K containing S-**1e**···BF$_3$. Bands pointing downwards are assigned to S-**1e**···BF$_3$. Bands pointing upwards indicate formation of an unknown species. * IR bands assigned to T-**4**, ° IR bands assigned to **8**.

Computational Studies. In a recent benchmark study of halogen-bonded systems, Kozuch et al. concluded that the CT character of these system requests functionals with a high amount of exact exchange such as M06-2X and ωB97X.[30] We therefore used both functionals for calculations of IR spectra and relative energies of carbene **4** and the product formed upon reaction with BF$_3$ (for simplicity the ωB97X results are only shown in the SI). Effects of the argon matrix were simulated by using the IEF-PCM, which resulted in small shifts in the calculated IR frequencies and energies. In general, the calculated IR spectra of the various species are in very good agreement with the experimental spectra, and inclusion of IEF-PCM(argon) corrections results in noticeable further improvement. DFT-calculated energies were compared to energies from single point CCSD(T) calculations.

The adiabatic S-T energy gap of **4** was calculated to -10.4 kcal/mol (including ZPVE corrections) at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory. The argon matrix contributes only by 0.1 kcal/mol to this value and is therefore negligible. With the same method, the S-T gap of diphenylcarbene **5** is computed to -5.8 kcal/mol, in reasonable agreement with experimental values.[31-32] Frenking et al. calculated a much smaller S-T gap for **4** of only -2.2 kcal/mol at BP86/def2-TZVPP[33] which demonstrates that the computed values highly depend on the functional selected. Single point CCSD(T)/6-311++G(d) calculations at the M06-2x geometries yield 3.7 kcal/mol which is presumably more reliable (Figure 4).

According to our computations (CCSD(T)/6-311++G(d)//M06-2x/6-311++G(d)/IEF-PCM(argon), T-**4** interacts only weakly with BF$_3$ with a binding energy of 6.4 kcal mol^{-1}. In contrast, the reaction of S-**4** with BF_3 to form the Lewis acid-base complex **1e** is strongly exothermic, releasing almost 29 kcal mol^{-1}, despite the formation of a zwitterion with a destabilized cyclopentadienyl cation fragment (Figure 4). The singlet state S-**1e** is calculated to be 2.3 more stable than the triplet state T-**1e**. Various DFT levels predict S and T to be nearly degenerate or T being ground state (Figure S10, Tables S1 and S2).

The complex S-**1e**...BF_3 bearing two BF_3 molecules shows a highly unusual bonding pattern. The second BF_3 is bound via a fluorine atom that bridges the two BF_3 units with almost equal bond distances to the two adjacent boron atoms (Figure 5). This results in a strong binding energy of the second BF_3 of 19.0 kcal mol^{-1} at the CCSD(T)/6-311++G(d)//M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory. The bridging fluorine atom shows almost equal bond distances to the R-BF_2 unit (1.552 Å) and the terminal BF_3 (1.596 Å), which is clearly longer than that of BF_4^- (1.408 Å) calculated at the same level of theory (Figure 6). In the IR spectrum, the fluorine bridge leads to a characteristic band at 537 cm^{-1} which is assigned to the asymmetric F-B-F stretching vibration. The calculations reveal that the bridging fluorine atom in S-**1e**...BF_3 carries less negative charge than the other fluorine atoms and thus exhibits the character of a rare fluoronium bridge. Similar species are cations with fluoronium bridging two carbon atoms,[34] or two silicon atoms.[35] The complex S-**1e**...BF_3 is the only structure we found in our attempts to add a second molecule of BF_3 to S-**1e**. Other structures are either no minima or weakly bound van der Waals complexes.

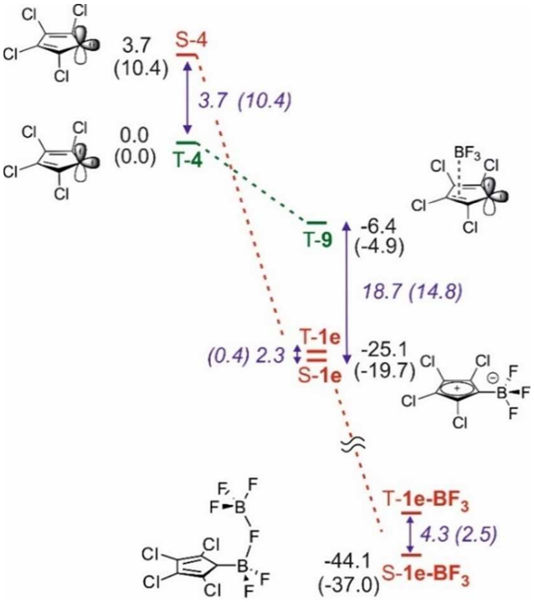
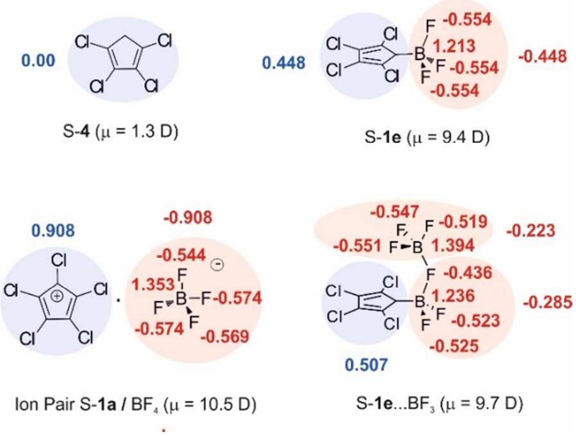


Figure 4. Energy diagram showing the S-T gaps (kcal mol^{-1}) of **4** and its most stable complexes with BF_3 calculated at the CCSD(T)/6-311++G(d)//M06-2x/6-311++G(d)/IEF-PCM (argon) level of theory. Values between parenthesis correspond to M06-2x/6-311++G(d)/IEF-PCM (argon) level of theory.

Chart 3. NBO charges and dipole moments[a]



[a]Calculated at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory.

The charge separation in S-**1e** and S-**1e**...BF_3 resulting in cyclopentadienyl cation fragments can be verified spectroscopically: the frequency of the E symmetrical B-F stretching vibration in BF_3 strongly correlates with the charge at BF_3 and can be used to estimate the charge distribution(Figure S8).[28] An analysis of this vibration in S-**1e** indicates a negative charge at the BF_3 moiety. The charge separation is also indicated by the computed high dipole moment of 9.4 D for S-**1e**, compared to 1.3 D for S-**4** and 10.5 D for the ion pair between cation **1c** and BF_4^- (Chart 3). The NBO charges reveal a charge separation of 0.45 between the cyclopentadienyl and the BF_3 units, half of that of the ion pair.

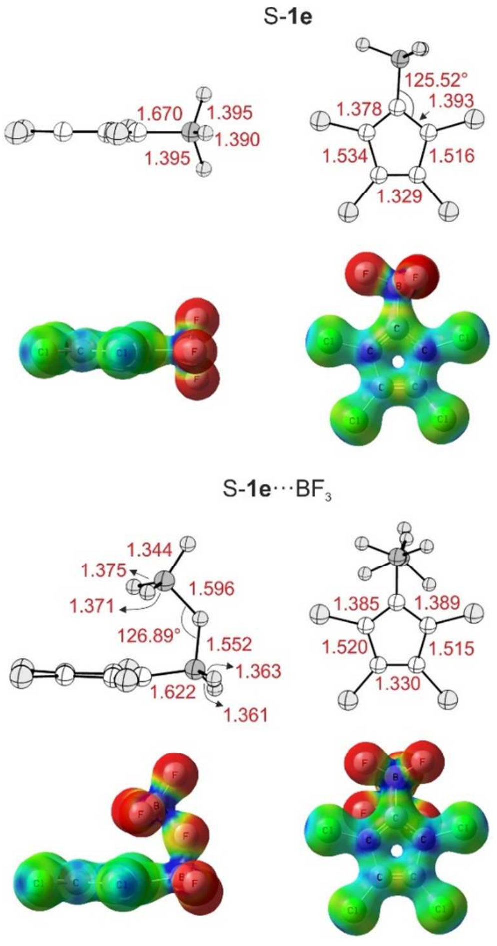


Figure 5. Some structural parameters of the optimized structures of S-**1e** and S-**1e**$\cdots$BF$_3$ computed at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory. Plots of electrostatic potential (isosurface value 0.05) of S-**1e** and S-**1e**$\cdots$BF$_3$ are shown on the bottom (blue: positive potential, red: negative potential).

Main criteria of aromaticity and antiaromaticity are (i) energetic, (ii) structural, and (iii) magnetic.[36] The energetic stabilization strongly depends on a suitable reference system, and we therefore discuss here the antiaromaticity of S-**1e** only with respect to the latter two criteria. While structural (as well as all other) criteria have been criticized to be distinctive for aromatic compounds, we expect that an aromatic state of the same molecule shows much less bond alternation than an antiaromatic states with large Jahn-Teller distortion. The variations of bond lengths in the cyclopentadienyl units of T-**1e**, S-**1e** and S-**1e**$\cdots$BF$_3$ can be correlated to the A parameter as defined by Julg and François.[37-38] For T-**1e**, S-**1e**, and S-**1e**$\cdots$BF$_3$ the calculated A values are 0.99, 0.29 and 0.36, respectively, in perfect agreement with the values determined for the corresponding electronic states of the parent cyclopentadienyl cation **1a** by Wright and Lee.[39] Based on these results, T-**1e** has an aromatic character, while S-**1e** and S-**1e**$\cdots$BF$_3$ are clearly *anti*aromatic molecules. The bond distances (Figures 5 and 6) suggest that S-**1e** and S-**1e**$\cdots$BF$_3$ are better described as the allylic form, in contrast to the singlet state of **1a**, for which the dienylic form is computed to be more stable.[21, 40]

The computed NICS(0)[41] values are -2.0, 38.2 and 35.0 for T-**1e**, S-**1e** and S-**1e**$\cdots$BF$_3$ respectively, again confirming the *anti*aromaticity of S-**1e** and S-**1e**$\cdots$BF$_3$. However, the antiaromatic character of the cation fragments in the zwitterions is partially reduced compared to the cations, as indicated by the NICS(0) values of 97.1 of S-**1a**, -0.8 for T-**1a**, 60.3 for S-**1c**, and -2.4 for T-**1c**. The anisotropy of the induced current density (ACID) is also a helpful method to investigate and visualize the delocalization of electrons in a molecule.[42] The ACID scalar field isosurfaces of S-**1e** and S-**1e**$\cdots$BF$_3$ clearly show paratropic ring currents, while a diatropic ring current is observed for T-**1e** (Figure 6). Thus, the ACID plots confirm that S-**1e** and S-**1e**$\cdots$BF$_3$ are *anti*aromatic molecules.

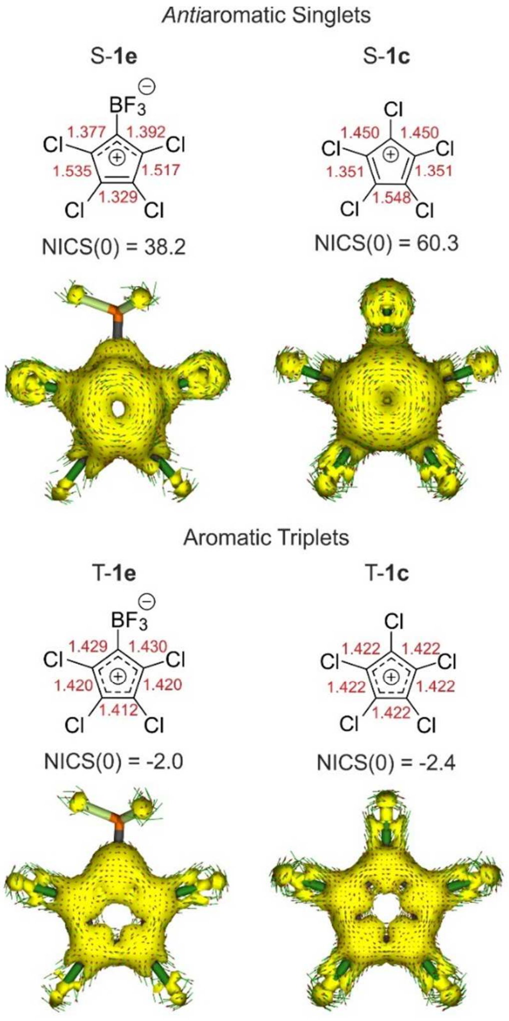


Figure 6. ACID isosurface (value 0.05), NICS(0) values and bond lengths in the five-membered ring (Å) of S-**1e**, T-**1e**, S-**1c**, T-**1c** computed at the M06-2x/6-311++G(d)/IEF-PCM(argon) level of theory. The current density vectors indicate the direction of the ring current. S-**1e** and S-**1c** show paratropic (anti-clockwise) currents, indicating its strong antiaromatic character, whereas T-**1e** and T-**1c** show diatropic currents indicative for aromaticity.

Conclusion

Singlet carbenes are strong Lewis bases, and their interactions with BF_3 as a strong Lewis acid results in the barrierless, exothermic formation of zwitterions with the former carbene unit bearing a positive charge and a negatively charged BF_3 unit. For singlet diphenylcarbene, the energy of the interaction with BF_3 under formation of a zwitterion containing a benzhydryl cation unit was calculated to approximately 35 kcal/mol.[28] The large exothermicity of reactions of carbenes with BF_3 allows to synthesize zwitterions with highly destabilized cations as units bearing the positive charge. Based on this concept, we developed an efficient synthesis of an antiaromatic molecule under the very mild conditions of matrix isolation at cryogenic temperatures.

The zwitterion S-**1e** and its BF_3 complex S-**1e**⋯BF_3 consist of cyclopentadienyl cation fragments which show the essential properties of a 4 π-electron antiaromatic molecule: (i) singlet ground state, (ii) strong bond alternation, (iii) large positive NICS(0) value and (iv) paratropic ring current. The IR spectrum is consistent with an allylic rather than a dienylic form of the cyclopentadienyl unit. In the parent cyclopentadienyl cation **1a**, the dienylic form was calculated as minimum and the allylic form as low-barrier (0.35 kcal/mol) transition state of the pseudorotation process.[21, 40] In S-**1e** with a lower C_{2v} symmetry the structure is locked into the allylic form. Despite this considerable distortion, the zwitterion retains a considerable amount of antiaromatic character. While S-**1e** is highly photolabile, S-**1e**⋯BF_3 is stabilized by the second BF_3 molecule via a highly unusual B-F-B fluoronium bridge.

In a Feature Article in 2009, Stanger asked “What is aromaticity: …can it really be defined?” and answered “… with the current state of knowledge, the answer to the question posed in the title has to be negative.” This is even more true for antiaromaticity, as nicely shown in the debate on whether tetrafluoro cyclobutadiene is antiaromatic or rather aromatic.[3] Despite its fuzzy definition, antiaromaticity will remain to be a highly useful concept in chemistry. Therefore, the isolation and spectroscopic characterization of molecules such as **1e** that clearly fulfill the criteria of antiaromaticity are important to keep the concept of antiaromaticity alive.

Experimental Section

Materials. All chemicals and solvents were used as received without further purification. Most compounds were purchased from Sigma Aldrich if not noted otherwise. Hexaclorocyclopentadien, hydrazine hydrate were purchased from commercial sources.

Tetrachlorodiazocyclopentadiene (**7**). Tetrachlorocyclopentadienonehydrazone was synthesized and purified according to a literature procedure starting from hexachlorocyclopentadiene.[43]

Calculated: N:12.08 C:26.07 H:0.86 Found: N:12.02 C:26.03 H:0.92

Tetrachlorodiazocyclopentadiene was synthesized by oxidation of tetrachlorocyclopentadienonehydrazone with Ag_2O.[44]

Calculated: N:12.18 C:26.12 H:0 Found: N:12.6 C:26.1 H:0.55

IR (Ar), ν (cm^{-1}): 2107 (N_2); 1590, 1407, 1396, 1277, 1264, 1253, 1086 (C-C); 778, 739 (C-Cl).

IR spectroscopy. Matrix isolation experiments were performed by standard techniques using Sumitomo Heavy industries two-staged closed-cycle helium cryostats (cooling power 1 W at 4 K) to obtain temperatures around 3 K. The matrices were generated by co-deposition of tetrachlorodiazocyclopentadiene and 1% of BF_3 with a large excess of argon, xenon or neon for generating the corresponding matrices on top of a cold CsI window at 3 K. A flow rate of approximately 1.80 sccm was used for the deposition of the matrix. Tetrachlorocyclopentaylidene T-**4** was generated by photolysis of **7** at 3 K using LED source at $\lambda = 450$ nm. Irradiation at $\lambda = 450$ nm and $\lambda = 365$ nm were performed by using LED sources. FTIR spectra were recorded in the range between 400 and 4000 cm^{-1} with 0.5 cm^{-1} resolution for xenon and argon matrices, while a resolution of 0.25 cm^{-1} was used for neon matrices.

UV-Vis spectroscopy. Matrix UV-Vis spectra were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer in the range of 200 – 800 nm with a resolution of 0.1 nm. Argon matrices were generated by co-deposition of tetrachlorodiazocyclopentadiene **7** and 1% of BF_3 with a large excess of argon, xenon or neon for generating the corresponding matrices on a sapphire window cooled to 8 K.

Computational Methods. All gas phase DFT geometry optimizations and frequency calculations were carried out using the M06-2x[45] and wB97X-D[46] functionals in combination with the integral equation formalism of the polarizable continuum model (IEF-PCM).[47] The 6-311++G(d) polarized valence-triple-ξ basis set were employed for both functionals.[48-49]. All DFT calculations were performed by using Gaussian 09 revision D.01.[50] Single point energies were calculated at the CCSD(T)/6-311++g(d)//M06-2x/6-311++g(d)/IEF-PCM(argon) level of theory. The CCSD(T) single point calculations were performed using the Molpro[51] software. For open-shell species, the CCSD(T) energies were calculated using the partially spin restricted (RHF-RCCSD) open-shell coupled cluster formalism implemented in Molpro.

ASSOCIATED CONTENT

Supporting Information

Experimental details, additional figures and tables. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

Wolfram Sander. Email: wolfram.sander@rub.de

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft (DFG). We thank Prof. Rainer Herges for giving us access to the ACID program.

REFERENCES

1. Breslow, R., *Chem. Eng. News* **1965,** *43*, 90-100.
2. Breslow, R., *Chem. Rec.* **2014,** *14*, 1174-1182.
3. Koehler, F.; Herges, R.; Stanger, A., *J. Phys. Chem. A* **2007,** *111*, 5116-5118.
4. Allen, A. D.; Tidwell, T. T., *Chem. Rev.* **2001,** *101*, 1333-1348.
5. Wu, J. I. C.; Mo, Y. R.; Evangelista, F. A.; Schleyer, P. v. R., *Chem. Commun.* **2012,** *48*, 8437-8439.
6. Kass, S. R., *J. Org. Chem.* **2013,** *78*, 7370-7372.
7. Breslow, R.; Chang, H. W.; Yager, W. A., *J. Am. Chem. Soc.* **1963,** *85*, 2033-2034.
8. Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E., *J. Am. Chem. Soc.* **1967,** *89*, 1112-19.
9. Breslow, R.; Hill, R.; Wasserman, E., *J. Am. Chem. Soc.* **1964,** *86*, 5349-50.
10. Vančik, H.; Novak, I.; Kidemet, D., *J. Phys. Chem . A* **1997,** *101*, 1523-1525.
11. Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffmann, J. M., Jr.; Perchonock, C.; Wasserman, E.; et, a., *J. Am. Chem. Soc.* **1973,** *95*, 3017-18.
12. Baird, N. C., *J. Am. Chem. Soc.* **1972,** *94*, 4941-&.
13. Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R., *Angewandte Chemie International Edition* **1998,** *37*, 1945-1948.
14. Worner, H. J.; Merkt, F., *Angew. Chem. Int. Ed.* **2006,** *45*, 293-296.
15. Worner, H. J.; Merkt, F., *J. Chem. Phys.* **2007,** *127*, 034303.
16. Vancik, H.; Novak, I.; Kid-emet, D., *J. Phys. Chem. A* **1998,** *102*, 8437-8438.
17. Reindl, B.; Schleyer, P. v. R., *J. Comput. Chem.* **1998,** *19*, 1402-1420.
18. Lee, E. P. F.; Wright, T. G., *Phys. Chem. Chem. Phys.* **1999,** *1*, 219-225.
19. Zilberg, S.; Haas, Y., *J. Am. Chem. Soc.* **2002,** *124*, 10683-10691.
20. Alonso, M.; Herradon, B., *Phys. Chem. Chem. Phys.* **2010,** *12*, 1305-1317.
21. Zou, W.; Filatov, M.; Cremer, D., *Int. J. Quantum Chem.* **2012,** *112*, 3277-3288.
22. Iversen, K. J.; Wilson, D. J. D.; Dutton, J. L., *Chem. - Eur. J.* **2014,** *20*, 14132-14138.
23. Costa, P.; Sander, W., *Angew. Chem. Int. Ed.* **2014,** *53*, 5122-5125.
24. Costa, P.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W., *J. Am. Chem. Soc.* **2014,** *136*, 15625-30.
25. Costa, P.; Trosien, I.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W., *Angew. Chem. Int. Ed.* **2015,** *54*, 2656-2660.
26. Henkel, S.; Costa, P.; Klute, L.; Sokkar, P.; Fernandez-Oliva, M.; Thiel, W.; Sanchez-Garcia, E.; Sander, W., *J. Am. Chem. Soc.* **2016,** *138*, 1689-1697.
27. Knorr, J.; Sokkar, P.; Schott, S.; Costa, P.; Thiel, W.; Sander, W.; Sanchez-Garcia, E.; Nuernberger, P., *Nat. Commun.* **2016,** *7*, 12968.
28. Costa, P.; Mieres-Perez, J.; Ozkan, N.; Sander, W., *Angew. Chem. Int. Ed.* **2017,** *56*, 1760-1764.
29. Bell, G. A.; Dunkin, I. R., *J. Chem. Soc. Faraday II* **1985,** *81*, 725-734.
30. Kozuch, S.; Martin, J. M. L., *J. Chem. Theory Comput.* **2013,** *9*, 1918-1931.
31. Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y., *Tetrahedron* **1985,** *41*, 1543-1554.
32. Sitzmann, E. V.; Langan, J. G.; Griller, D.; Eisenthal, K. B., *Chem. Phys. Lett.* **1989,** *161*, 353-60.
33. Goedecke, C.; Leibold, M.; Siemeling, U.; Frenking, G., *J. Am. Chem. Soc.* **2011,** *133*, 3557-3569.
34. Struble, M. D.; Scerba, M. T.; Siegler, M.; Lectka, T., *Science* **2013,** *340*, 57.
35. Panisch, R.; Bolte, M.; Müller, T., *J. Am. Chem. Soc.* **2006,** *128*, 9676-9682.
36. Stanger, A., *Chem. Commun.* **2009**, 1939-1947.
37. Julg, A.; François, P., *Theoret. Chim. Acta* **1967,** *8*, 249-259.
38. Giambiagi Myriam, S. d.; Giambiagi, M.; Figueiredo Aloysio Paiva, d., Revisiting Julg's Structural Approach to Aromaticity. In *Zeitschrift für Naturforschung A*, 2001; Vol. 56, p 413.
39. P. F. Lee, E.; G. Wright, T., *Phys. Chem. Chem. Phys.* **1999,** *1*, 219-225.
40. Lo, P.-K.; Lau, K.-C., *J. Phys. Chem A* **2014,** *118*, 2498-2507.
41. Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T., *J. Am. Chem. Soc.* **1997,** *119*, 7075-7083.
42. Geuenich, D.; Hess, K.; Köhler, F.; Herges, R., *Chem. Rev.* **2005,** *105*, 3758-3772.
43. Klages, F.; Bott, K., *Chem. Ber.* **1964,** *97*, 735-740.
44. Reimer, K. J.; Shaver, A.; Quick, M. H.; Angelici, R. J., Halocyclopentadienyl Complexes of Manganese and Rhodium. In *Inorganic Syntheses*, John Wiley & Sons, Inc.: 1980; pp 188-196.
45. Zhao, Y.; Truhlar, D. G., *Acc. Chem. Res.* **2008,** *41*, 157-67.
46. Chai, J.-D.; Head-Gordon, M., *Physical Chemistry Chemical Physics* **2008,** *10*, 6615-6620.
47. Tomasi, J.; Mennucci, B.; Cammi, R., *Chem Rev* **2005,** *105*, 2999-3094.
48. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., *Journal of Chemical Physics* **1980,** *72*, 650-654.
49. McLean, A. D.; Chandler, G. S., *The Journal of Chemical Physics* **1980,** *72*, 5639-5648.
50. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09 Rev. B01*, Revision B.01; Gaussian, Inc.: Wallingford CT, 2010.

51. Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M., *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2012,** *2*, 242-253.

SYNOPSIS TOC