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Moritz Malischewski, Konrad Seppelt. Isolation and Characterization of a Non-Rigid Hexamethylbenzene-SO₂⁺ Complex. *Angewandte Chemie International Edition*, 2017, 56 (52), pp.16495-16497. 10.1002/anie.201708552 . hal-01730776

HAL Id: hal-01730776

<https://hal.sorbonne-universite.fr/hal-01730776>

Submitted on 13 Mar 2018

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Isolation and characterization of a non-rigid hexamethylbenzene-SO²⁺ complex

Moritz Malischewski^{[a],[b]} and Konrad Seppelt^[a]

In memoriam of George Olah (1927-2017)

Abstract: During our preparation of the pentagonal-pyramidal hexamethylbenzene-dication C₆(CH₃)₆²⁺ we isolated the unprecedented dicationic species C₆(CH₃)₆SO²⁺ (AsF₆⁻)₂ from the reaction of hexamethylbenzene with a mixture of anhydrous HF, AsF₅ and liquid SO₂. This compound can be understood as a complex of unknown SO²⁺ with hexamethylbenzene. Herein, we report the synthesis, its molecular structure and its spectroscopic characterization.

Sulfur dioxide SO₂ is a toxic gas, which is annually produced in million ton scale during the production of sulfuric acid. Aqueous solutions of SO₂ are weakly acidic and behave as a reducing agent. In contrast, anhydrous SO₂ (boiling point -10°C) can be used as an extremely oxidation-stable solvent (up to nearly +6 V vs. standard hydrogen electrode).^[1] In the past years, activation of small molecules has become an important research field in inorganic chemistry, although reports on the reactivity of SO₂ are scarce. The most successful approach so far has been the use of frustrated Lewis pairs^[2-3] to overcome the weak nucleophilicity of SO₂, which even allows its use as a solvent in superacid chemistry. For instance, Gillespie stated that SO₂ is not protonated to a significant extent in magic acid (HSO₃F/SbF₅).^[4] However, Kornath reported 30 years later the formation of [FS(OH)₂]⁺ SbF₆⁻ from the reaction of SO₂ with HF/SbF₅.^[5]

In order to oxidize hexamethylbenzene C₆(CH₃)₆ to its pentagonal-pyramidal dication C₆(CH₃)₆²⁺,^[6] we used the powerful oxidant and Lewis acid AsF₅ in a mixture of anhydrous HF and liquid SO₂ as solvent. Surprisingly, instead of the desired product, orange crystals of C₆(CH₃)₆SO²⁺ (AsF₆⁻)₂ could be isolated in the cold from the orange-red solution. In the absence of the superacid HF/AsF₅ no reaction is observed. When colourless hexamethylbenzene is dissolved in pure SO₂ only a yellow solution is obtained, probably due to the formation of a weak charge-transfer complex. The increased electron density on the oxygen atoms of SO₂ in this complex enhances the proton affinity of SO₂ (see supporting information for further details) and therefore facilitates protonation by the superacid HF/AsF₅ which leads to the abstraction of one oxygen atom as H₃O⁺. Consequently, SO₂ is formally cleaved into SO²⁺ and O²⁻. The former binds to the electron-rich hexamethylbenzene while the latter is consumed by the (super/Lewis) acid.

However, under the reaction conditions no pure material is obtained since side reactions occur (e.g. protonation of hexamethylbenzene) which complicate the spectroscopic characterization. Due to the sensitivity of the complex no work-

up besides recrystallization directly from the reaction mixture is possible. Although C₆(CH₃)₆SO²⁺ (AsF₆⁻)₂ is the main component of the isolated material, ionic side-products co-precipitate due to their low solubility in HF at low temperatures.



Figure 1. Preparation of C₆(CH₃)₆SO²⁺ (AsF₆⁻)₂

C₆(CH₃)₆SO²⁺ (AsF₆⁻)₂ crystallizes in the triclinic space group P-1. The dication consists of an almost planar benzene ring capped by a sloped SO fragment. The sulfur atom is coordinated to a former aromatic C-C bond (bond length 1.438(5) Å). All other C-C bond lengths of the benzene ring are in the range of 1.396(6)-1.441(5) Å (mean value 1.423 Å) and are therefore only slightly elongated compared to the average C-C-bond length in hexamethylbenzene (1.411(1) Å).^[7]

The carbon-sulfur distances are 2.121(3) and 2.167(3) Å and therefore significantly longer than carbon-sulfur single bonds in thiirane (ethylene sulfide) with 1.82 Å.^[8] Interestingly, the C-S-C bond angle is compressed to 39.69(14)° and therefore even smaller than in three-membered thiirenium and thiiranium salts (40.9(1)-47.6(2)°).^[9] The distance between the sulfur atom and the benzene plane is 1.941 Å while it is 2.110 Å to the benzene centroid. This indicates that at least in the solid state the SO ligand is not located symmetrically in the middle of the benzene ring. The other carbon-sulfur distances are in the range of 2.376-2.991 Å and therefore significantly below of the sum of van-der-Waals radii (3.5 Å).^[10]

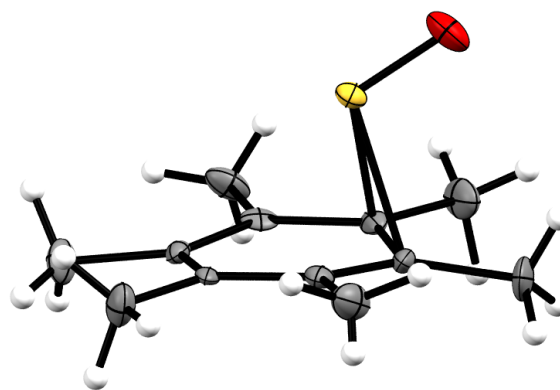


Figure 2. Molecular Structure of C₆(CH₃)₆SO²⁺, S yellow, O red, C grey, H white

The sulfur-oxygen bond length of 1.424(2) Å is characteristic for a relatively short S-O double bond.^[11] This value is lower compared to the double bond in free SO (1.481 Å, triplet ground state, isovalence-electronic to O₂),^[12] but higher than the calculated literature value of 1.39 Å for a triple bond in free SO²⁺,^[13] because the charge-transfer into an antibonding S-O orbital of SO²⁺ lowers the S-O bond order. This trend is additionally reflected by DFT calculations using B3LYP/def2-TZVP (S-O bond length of 1.376 Å for SO²⁺ and 1.438 Å for C₆(CH₃)₆SO²⁺).

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Table 1. Selected geometrical parameters of $C_6(CH_3)_6SO^{2+}(AsF_6^-)_2$ in the crystal

Geometrical parameter	$C_6(CH_3)_6SO^{2+}(AsF_6^-)_2$
C-C bond lengths (benzene ring)	1.396(6)-1.438(5) Å
C-S bond distances	2.121(3), 2.167(3) Å 2.376-2.991 Å
C-S-C bond angle	39.69(14)°
S-O bond length	1.424(2) Å

DFT calculations for the S-O vibration using B3LYP/def2-TZVP predicted a value of 1266 cm^{-1} for the SO^{2+} adduct, and 1541 cm^{-1} for free SO^{2+} , respectively, indicating a lower bond order for the charge-transfer complex. The S-O vibration of free SO is experimentally known (1137 cm^{-1}).^[14]

An IR-spectrum of the isolated material revealed a strong band at 1250 cm^{-1} which can be assigned to the S-O stretch vibration.^[15]

Table 2. Comparison of experimental and calculated S-O distances for $C_6(CH_3)_6SO^{2+}$, SO and SO^{2+}

Compound	S-O distance in Å (exp.)	S-O distance in Å (calc.)	S-O vibration in cm^{-1} (exp.)	S-O vibration in cm^{-1} (calc.)
$C_6(CH_3)_6SO^{2+}$	1.424	1.438	1250	1266
SO	1.481	1.490	1137	1159
SO^{2+}	-----	1.376	-----	1541

In contrast to SO_2 or SO_3 , lower-valent sulfur oxides are generally unstable. Free SO even decomposes in high dilution in the gas phase within short time^[16] but can be detected in interstellar space.^[17] Interestingly, SO can be stabilized as a ligand in the coordination sphere of metal complexes.^[16, 18-19] In general, the μ^2 bridging mode^[20] is much more often observed than SO as a terminal^[21] or μ^3 bridging ligand.^[22] Recently, adduct formation of SO with carbenes has been reported.^[23-24]

For SO^{2+} , which is iso-valence-electronic to N_2 , CO and NO^+ , literature reports are extremely rare. In the 1930s Jander discussed the autodissociation of liquid SO_2 into SO^{2+} and SO_3^{2-} .^[25] Later reports claimed the existence of solvated SO^{2+} from the reaction of thionyl chloride and silver salts in acetone^[26] and from autodissociation of thionyl chloride in DMF.^[27] Under strongly ionizing conditions, SO^{2+} has been detected in the gas phase.^[28]

Although the detection of the $C_6(CH_3)_6SO^{2+}$ adduct is unprecedented, the general structure is not. Already in the 1980s, the formation of a charge-transfer complex between NO^+

and hexamethylbenzene was observed.^[29] NO^+ is coordinated to two carbon atoms of an aromatic C-C bond and tilted in respect to the benzene plane. The distance between the nitrogen atom and the benzene plane is with 2.07 Å slightly longer than in the SO^{2+} adduct. The N-O bond in $[C_6(CH_3)_6NO]^+ SbF_6^-$ ($1.108(2)\text{ Å}$)^[7, 30] is slightly elongated compared to NO^+ ($1.062(4)\text{ Å}$).^[31]

The similarity between the NO^+ and SO^{2+} adducts is reflected by ^{13}C NMR spectra. While the two signals of hexamethylbenzene shift from δ 17.0 and 133.2 ppm to 17.8 and 150.8 ppm in the NO^+ complex,^[30] the SO^{2+} adduct gives two signals at δ 20.8 and 165.5 ppm (measured in SO_2 at $-70^\circ C$) which proves the dynamic nature of the complex as well as the deshielding of the carbon atoms of the benzene ring.

This dynamic behaviour can be described with three different structures: a three-membered ring, a C_s symmetric transition state and a pyramidal isomer. According to theoretical calculations with MP2/cc-pVTZ the energy difference between these three isomers for $C_6(CH_3)_6SO^{2+}$ is $\leq 1\text{ kJ/mol}$ (see supporting information). This calculated barrier would be one of the smallest known for fluxional molecules.^[32] So the SO moiety can move practically without barrier over the benzene ring. Consequently, the same should be true for $C_6H_6SO^{2+}$ since $C_6H_6NO^+$ is also known to have a very flat potential energy surface.^[33] For comparison, ethane C_2H_6 has a rotational barrier of about 13 kJ/mol . The heavier homologues Si_2H_6 and Ge_2H_6 have rotational barriers of about 4 and 3 kJ/mol .^[34]

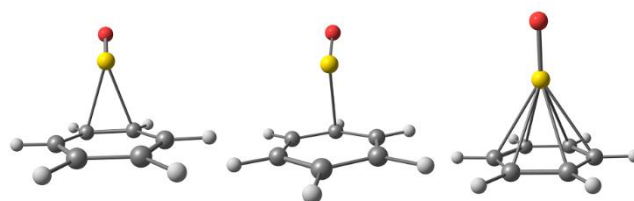


Figure 3. Calculated structures for $C_6H_6SO^{2+}$, left: three-membered ring, middle: transition state (both with C_s symmetry), right: pyramidal structure

It is noteworthy, that similar behaviour, namely the dynamic rearrangement of a sulfur-monoxide-(tetrakis-trifluoromethyl)-cyclobutadiene adduct to the corresponding cyclobutene-sulfoxide was reported only to be frozen at cryogenic temperatures around $-151^\circ C$.^[35-36]

In summary, $C_6(CH_3)_6SO^{2+}(AsF_6^-)_2$ can be prepared from the reaction of hexamethylbenzene with a mixture of anhydrous HF, AsF_5 and liquid SO_2 . Although $[C_6(CH_3)_6SO]^{2+}$ can only be handled in SO_2 or HF (due to decomposition in organic solvents) its existence suggests the possibility of stabilizing highly electrophilic small molecules as charge-transfer complexes with permethylated arenes. The SO moiety is supposed to migrate over the benzene ring with almost no energetic barrier.

Experimental Section

The reaction is performed in PFA tubes (tetrafluoroethylene-perfluoroalkoxyvinyl-copolymer) connected to stainless steel valves / stainless steel vacuum line. Attention: SO_2 , HF and AsF_5 are highly toxic gases which should only be handled by trained personal in appropriate equipment.

Thionylhexamethylbenzenium(2+)-hexafluoroarsenate
Thionylumhexamethylbenzene(2+)-hexafluoroarsenate

41 mg (0.25 mmol) hexamethylbenzene are filled into a 8 mm PFA-tube. 0.6 g SO₂ are condensed in at -196°C. The mixture is thawed to obtain a yellow solution. Subsequently, the mixture is cooled to -196°C and 2.4 g anhydrous HF and 0.2 g (1.2 mmol) AsF₅ are condensed in. The tube is sealed off and placed in a -75°C freezer. After one day, the tube is brought to room temperature and shaken for some minutes (Attention: overpressure!) and then placed again in the freezer. After several days orange needles are obtained in the orange-red solution. The crystals are decanted off in the sealed tube by turning the tube carefully upside down, the mother liquor is frozen with liquid nitrogen. The tube is opened with a scissor and the open tube containing the crystalline material is connected to a steel valve and dried in vacuum, the mother liquor is discarded (Attention: Danger!). The amount of isolated product is low to moderate.

NMR (SO₂, -70 °C, unlocked) ¹H: δ 3.13 ppm (s, br, 18H); 10.36 ppm (s, br, H₃O⁺)

¹³C[¹H]: δ 20.76 ppm (CH₃, 6 C), 165.46 ppm (ring, 6 C)

¹⁹F: δ -56.23 ppm (br, AsF₆⁻)

IR in cm⁻¹: 2915, 1592, 1516, 1433, 1377, 1338, 1250, 1076, 1028, 990, 962, 693, 671

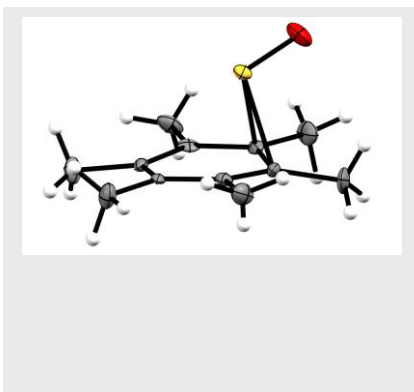
Acknowledgements

This work was supported by the Free University Berlin, Verband der Chemischen Industrie (VCI) and Deutsche Forschungsgemeinschaft (GRK 1582 (Fluorine as a Key Element)). M. M. acknowledges a postdoctoral fellowship by the German Research Foundation (DFG). Computing time was made available by High-Performance Computing at ZEDAT/FU Berlin. We thank Prof. Dr. Dieter Lentz for crystallographic help and Dr. Carsten Müller for creating a video of the dynamic migration of the SO moiety.

Keywords: carbocation • electron-deficient compounds • superacid • hypercoordination • oxidation

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The unprecedented complex $C_6(CH_3)_6SO^{2+}(AsF_6^-)_2$ is isolated from the reaction of hexamethylbenzene with SO_2 , anhydrous HF and AsF_5 .



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Isolation and characterization of a non-rigid hexamethylbenzene-SO²⁺ complex
