Oxidation of CS_2 by $AsBr_4^+$: The Unexpected Formation of the Simple $CS_2Br_3^+$ Carbenium Ion

Marcin Gonsior and Ingo Krossing*[a]

Abstract: During the preparation of $AsBr_4^+[Al(OR)_4]^-$, the novel carbocation $CS_2Br_3^+$ was synthesized by reaction of $AsBr_3$, Br_2, CS_2, and $Ag[Al(OR)_4]$ ($R = C(CF_3)_3$). $CS_2Br_3^+[Al(OR)_4]^-$ was characterized by its crystal structure, NMR and IR spectroscopy, and quantum chemical calculations (including COSMO solvation enthalpies). Additional experiments as well as the computed thermodynamics indicated two likely reaction pathways: $Ag^+ + 2Br_2 + CS_2 \rightarrow CS_2Br_3^+ + AgBr$ and the direct $4e^-$ oxidation reaction $AsBr_4^+ + CS_2 \rightarrow CS_2Br_3^+ + \frac{1}{6}As_6Br_6$. Both reactions were observed experimentally and were calculated to be exergonic in solution by -226 and $-56\,kJ\,mol^{-1}$ respectively. As a result of charge delocalization the C–S and C–Br distances in the cation are shortened by 0.06 to 0.08 Å; the S–Br distances are also slightly shortened indicating a delocalization of the charge also to the bromine atoms in the (S–)Br moieties. Based on an analysis of the cation–anion contacts as well as quantum chemical MP2 calculations, a delocalization model as a planar 10π electron system is discussed and the π molecular orbitals are given. It will be shown that the electronic situation of $CS_2Br_3^+$ is very close to that in CBr_3^+, that is, the properties of SBr moieties and Br atoms as π donors towards a formal C^+ center are comparable.

Keywords: arsenic · carbenium ion · carbon disulfide · oxidation · weakly coordinating anions

Introduction

In the last decade it was shown that the heavier main-group elements P–Sb, S–Te, and Cl–I are astonishingly good π donors towards a carbocation center.[1] Of all α-hetero substituents of non-metallic elements the best π-donors are the lone pair orbitals of nitrogen. Oxygen and sulfur lone pair orbitals show slightly weaker donating strength towards a carbenium center than nitrogen, and least stabilizing are those of the halogens.[2] Some structures of simple carbocations including O and S as α-heteroatoms are known, that is, salts of $(MeS)_2CSH^+$,[3] $C(OH)_3^+$,[4] $(MeO)_2COH^+$,[5] $(MeO)(MeS)CSH^+$,[6] and $C(SH)_3^+$.[7] However, the available information on carbenium ions with α-halogen atoms is scarce. Structurally characterized nonaromatic simple carbocations with C–X (X = F–I) bonds are limited to $(Me)_2CF^+$,[8] $(MeO)C(H)X^+$ (X = F, Cl),[9] $(NH_2)ClBrC^+$,[10] $(NH_2)Cl_2C^+$,[11] $(Me)NCH_2CH_2SCBr^+$,[12] $(Me)(NH_2)XC^+$ (X = Cl, Br),[13,14] and $(CH{=}CH)(MeN)_2CI^+$[15] shown in Figure 1. However, cations bearing an NR_2 group are better addressed as iminium salts.

For the completely halogen-substituted CX_3^+ ions it was predicted[1,2,16,17] that the stabilizing effect of the halogen substituent increases from F to I (in opposition to the earlier conclusions[18]). The theoretical prediction was confirmed by the synthesis[17] and crystal structure of a room-temperature stable CI_3^+ salt.[19] Also the crystal structures of its lighter homologues CCl_3^+ and CBr_3^+ have been published very recently.[20] In most simple and reactive carbocations, fluoro-

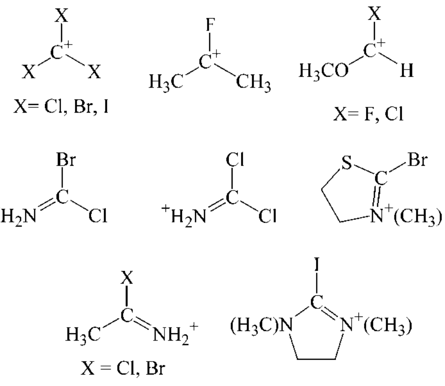

Figure 1. All known structurally characterized nonaromatic carbocations bearing a halogen substituent. The cations with NR_2 groups (R = H, Me, alkyl) are best interpreted as iminium salts.

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metallates of type MF_6^- and $M_2F_{11}^-$ (M = As, Sb) were used as weakly coordinating anions (WCA). By contrast, the CI_3^+ salt contains a new WCA—the fluorinated alkoxyaluminate $[Al(OR)_4]^-$ (R = $C(CF_3)_3$),[21] which is also used in the present work. In our continuing studies of the reactivity of the EX_2^+ ions (E = P, As) we fortuitously synthesized and fully characterized the novel $CS_2Br_3^+$ carbocation by the 4 e^- oxidation of CS_2 with $AsBr_4^+$. We will show that the $CS_2Br_3^+$ cation is electronically very close to the above-mentioned CBr_3^+. To the best of our knowledge, this is the first structural report of a carbocation that incorporates $C^+{-}S{-}X$ bonds (X = halogen). Only one report on the related marginally stable Cl_2CSX^+ (X = Cl, Br) ion, characterized by IR and NMR spectra, is available.[22]

Results

First synthesis of $CS_2Br_3^+[Al(OR)_4]^-$: Recently we prepared $AsBr_4^+[Al(OR)_4]^-$, which includes the $AsBr_4^+$ ion that was hitherto only structurally characterized by G. J. Schrobilgen et al. in $AsBr_4^+[FAs(OTeF_5)_5]^+$.[23] The $AsBr_4^+$ ion was first synthesized and characterized by Raman spectroscopy by Klapötke and Passmore.[24] $AsBr_4^+[Al(OR)_4]^-$ was prepared from $AsBr_3$, Br_2, and $Ag[Al(OR)_4]$ (R = $C(CF_3)_3$) in analogy to the PX_4^+ syntheses.[25] Full details of this reaction will be described elsewhere.[26] The reaction proceeds at low temperature in CH_2Cl_2 with precipitation of AgBr giving crystalline $AsBr_4^+[Al(OR)_4]^-$ in 54 % yield. However, when methylene chloride was replaced by a 1:1 mixture of CH_2Cl_2/CS_2, yellow crystals of a different shape than those of $AsBr_4^+$ precipitated from the cold concentrated filtrate in 50 % yield. The IR spectrum of those crystals did not contain the characteristic $AsBr_4^+$ band at 354 cm^{-1}[23] and, therefore, we decided to determine their crystal structure. The single-crystal X-ray determination showed the crystal to be $CS_2Br_3^+[Al(OR)_4]^-$ (**1**). The ^{13}C NMR spectrum of the same batch of crystals in CD_2Cl_2 at 213 K only showed a singlet at $\delta = 209.7$ ppm apart from the signals of the anion at $\delta = 120.5$ (q) and 78.0 ppm (broad). ^{13}C NMR spectra of $(MeS)_2CSH^+$,[3] $(MeO)(MeS)CSH^+$,[6] Cl_2CSCl^+,[21] and Cl_2CSBr^+[21] in SO_2 show signals assigned to the carbocation center in a similar range at $\delta = 221–231$ ppm. We attribute the small high-field shift of $\Delta(\delta\ ^{13}C)$ of 11–21 ppm in **1** to the presence of the heavy bromine atom at the carbenium center and the inverse halogen dependence of the shifts of compounds with a heavy halogen substituent.[16,27] Compound **1** is very sensitive to air and moisture, but is stable at room temperature in the solid state and for at least 20 h in CH_2Cl_2.

Crystal structure: The $CS_2Br_3^+[Al(OR)_4]^-$ salt (R = $C(CF_3)_3$, Figure 2) crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit ($Z = 8$).[28] Needle-shaped yellow crystals were obtained from a CH_2Cl_2/CS_2 mixture at −80 °C. The C−Br, C−S, S−Br distances of both independent cations ($CS_2Br_3^+$ #1 and $CS_2Br_3^+$ #2) and their average values together with relevant bond angles are given in Table 1. For comparison the MP2/TZVPP optimized structural parameters of gaseous $CS_2Br_3^+$ are also included.

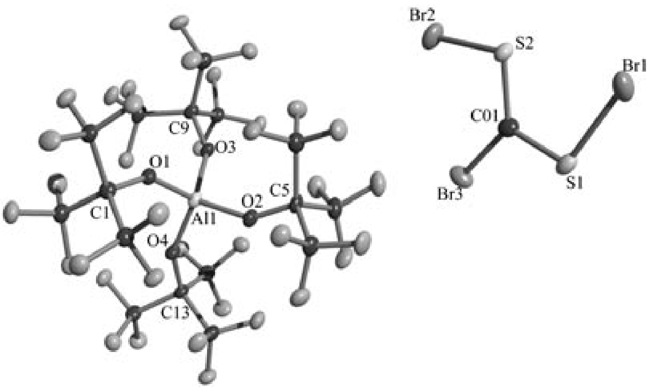


Figure 2. Section of the solid-state structure of $CS_2Br_3^+[Al(OR)_4]^-$ (R = $C(CF_3)_3$). For clarity only one cation–anion (#1) pair is shown (thermal ellipsoids drawn at the 25 % probability level).

Table 1. Experimental and calculated distances [Å] and angles [°] of the $CS_2Br_3^+$ ion.

$CS_2Br_3^+$ (#1)		$CS_2Br_3^+$ (#2)		Average	Calcd[a]
C01−S1	1.696(3)	C02−S3	1.702(3)	1.699(3)	1.690
C01−S2	1.669(3)	C02−S4	1.672(3)	1.671(3)	1.689
C01−Br3	1.817(3)	C02−Br6	1.819(3)	1.818(3)	1.838
S1−Br1	2.149(1)	S3−Br4	2.118(1)	2.133(1)	2.159
S2−Br2	2.139(1)	S4−Br5	2.159(1)	2.149(1)	2.148
Br2−Br3	3.401(3)	Br5−Br6	3.376(4)	3.389(4)	3.382
Br1−S2	3.083(3)	Br4−S4	3.122(3)	3.102(3)	3.130
Br3-C01-S1	111.76(2)	Br6-C02-S3	111.03(2)	111.40(2)	112.6
Br3-C01-S2	127.2(2)	Br6-C02-S4	127.5(2)	127.4(2)	125.9
S1-C01-S2	121.0(2)	S3-C02-S4	121.5(2)	121.3(2)	121.5
Br1-S1-C01	102.19(1)	Br4-S3-C02	103.14(1)	102.67(1)	103.1
Br2-S2-C01	105.64(1)	Br5-S4-C02	104.28(1)	104.96(1)	105.4

[a] MP2/TZVPP level.

Experimental and calculated structural parameters of the cation are in excellent agreement and deviate by less than 0.03 Å and 1.5°. The coordination of the carbenium centers in $CS_2Br_3^+$ is ideally planar as shown by the sum of the bond angles of 360.0°, but the $CS_2Br_3^+$ ions are slightly distorted from C_s symmetry with Br−S−C−Br torsion angles of 1.72(3)° to 2.58(3)° or 179.74(2)° to 179.75(2)°. The C−S distances of 1.669(3) to 1.702(3) Å are in the expected range and intermediate between a single and a double bond length (charge delocalization). However, there is a small but significant difference of about 0.028 Å in the length of the two sets of C−S bonds (vide infra). In $(MeS)_2CSH^+$[3] both equivalent C−S bonds (of the MeS group) are the same at about 1.682(8) Å, while in $C(SH)_3^+$ values from 1.683(5) to 1.712(6) Å[7] and in $(MeO)(MeS)CSH^+$[6] values between 1.692(7) and 1.702(7) Å were observed. The $CS_2Br_3^+$ ion includes the shortest C−S bond length (1.669(3) Å) of all sulfur-stabilized carbenium ions. Interestingly, the C−Br distance in **1** (1.818(3) Å, av.) is shortened in comparison to usual C−Br bond lengths by about 0.06 to 0.08 Å, that is, the Br atom is bonded to an sp^2-carbon with d(C−Br) = 1.881–1.899 Å.[29] By contrast, the C−Br distance in **1** is in good agreement with the C−Br bond length in the recently prepared CBr_3^+ ion (1.783(16)–1.851(16) Å, average 1.806(16) Å).[19] This shows that CBr_3^+ and $CS_2Br_3^+$ are electronically very similar and that the SBr group in $CS_2Br_3^+$ has a similar electronegativity and π-donor strength as a single Br atom in CBr_3^+. In the $CS_2Br_3^+$ ion, the S−Br distances are slightly on the short side and range from 2.118(1) to 2.159(1) Å relative to d(S−Br) = 2.169(2) Å[30] in Ph_3CSBr and 2.24 Å in S_2Br_2.[29] This indicates that the S−Br distance is also shortened as a result of the delocalization of the positive charge. The structural parameters of the anion are normal.[31,32] The cation–anion contacts of the two independent $CS_2Br_3^+$ ions in **1** are deposited as Supporting Information (Figure A). No strong contacts between the carbenium center and the anion are present. The strongest cation–anion contacts are found between the two S atoms as well as the (C−)Br atoms and the fluorine atoms of the anion (see Supporting Information). Using Brown's empirical formula[33] we calculated the partial charges residing on the sulfur atoms from the number and length of the fluorine contacts. Parameters for Br···F contacts are not available. The experimentally estimated partial charges together with the results of a population analysis of the calculated structure (MP2 level) are summarized in Table 2.

Table 2. Charge distribution in the $CS_2Br_3^+$ ion.

From lattice S···F contacts		Population analysis[b]	
atom in #1 (#2)	partial charge[a]	atom	partial charge
C01(C02)	–	C	+0.03
S1 (S3)	+0.30	S	+0.34
S2 (S4)	+0.23	S	+0.35
Br3 (Br6)	–	Br	+0.19
Br1 (Br4)	–	Br	+0.04
Br2 (Br5)	–	Br	+0.05

[a] Average charge on the both equivalent sulfur atoms. [b] Paboon = Population analysis based on occupation numbers.

From the estimated partial charges and also from the number and strength of the E···F contacts (E = S, Br), it follows that the positive charge is delocalized from the carbenium center primarily to the S and (C−)Br atoms. It should be noted that in contrast to the computational prediction the two strongest cation–anion contacts are directed towards the (C−)Br atoms (0.35 Å shorter than the sum of the van der Waals radii), while the shortest S−F contacts are only 0.25 to 0.27 Å shorter than the sum of the van der Waals radii. In summary we note that the positive charge in $CS_2Br_3^+$ is delocalized almost evenly among the S and (C−)Br atoms, while relatively little positive charge is transferred to the (S−)Br atoms. This is in qualitative agreement with the MP2 calculation.

In the solid state, the salt **1** forms a distorted CsCl structure with the almost spherical $[Al(OR)_4]^-$ ion forming a primitive cubic array and the $CS_2Br_3^+$ ions residing in the center of the cubic interstices (see Figures B and C in the Supporting Information).

Computational results: The total MP2 energy, zero-point energies, solvation energies as well as thermal and entropic contributions to the enthalpy and the free energy of all calculated species are collected in Table B in the Supporting Information. The optimized geometries of $CS_2Br_3^+$ (C_s), $AsBr_4^+$ (T_d), As_6Br_6 (D_{3d}), CS_2 ($D_{\infty h}$), and $AsBr_3$ (C_{3v}), but excluding Ag^+, AgBr, and Br_2, are deposited as Supporting Information in Figure D. Four additional isomers of $CS_2Br_3^+$, I (C_2), II (C_{2v}), III (C_2), and IV (C_{2v}), were also assessed (BP86/TZVPP, including vibrational analysis at the BP86/SVP level). They are shown in Figure 3.

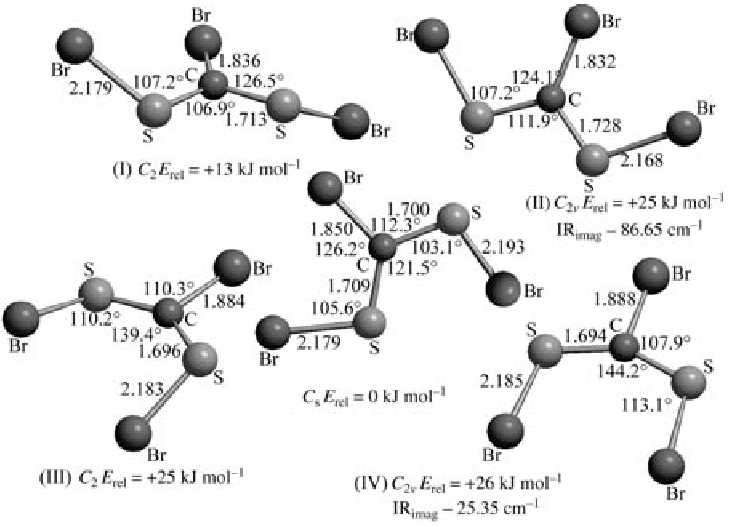


Figure 3. Isomers I–IV of the experimentally found $CS_2Br_3^+$ ion in the middle calculated at the BP86/TZVPP level. Relative energies (E_{rel}) are given in kJ mol^{-1}. Structures II and IV are transition states with one imaginary frequency. All other species are true minima.

The most favorable geometry of the isomers is the one found in the solid state (Figure 3, in the middle). All other isomers I to IV may be present in solution as intermediates.

Vibrational spectroscopy: The IR spectrum of a Nujol mull of crystalline **1** shows vibrations assigned to the anion $[Al(OR)_4]^-$ and weak bands assigned to the $CS_2Br_3^+$ ion. To enable a complete assignment, we calculated the vibrational frequencies of the $CS_2Br_3^+$ and $[Al(OR)_4]^-$ ions (BP86/SVP level), and simulated the spectra of **1** as well as the isolated anion as superposition of Gauss functions. Simulations and experimental spectra are shown in Figure E (see Supporting Information). Experimental and calculated frequencies of the cation of **1** are listed in Table 3.

In comparison to the simulated spectra only the vibrations at 257, 492, and 916 cm^{-1} can clearly be assigned to the cation. The calculated BP/SVP cation band at 960 cm^{-1} (MP2/TZVPP: 1057 cm^{-1}) is covered by the intense anion band at 973 cm^{-1}. The BP/SVP calculated bands at 377, 402, 409 cm^{-1} appear in the range 365–427 cm^{-1} as a shoulder of the 445 cm^{-1} anion band. The detailed assignment of the cation bands is given in Table 3. The band at 916 cm^{-1} is assigned to the C−Br stretch and may be compared to the C−Br vibration in the CBr_3^+ ion that was calculated by Schrobilgen et al. to appear at 932 cm^{-1} (no experimental data are available),[20] while MP2/TZVPP gave a value of 916 cm^{-1}. The band at 492 cm^{-1} is supposed to be the stretching vibration of the S–Br bond (S–$Br_{2/5}$); in Cl_2CSBr^+ a band at 492 cm^{-1} was assigned to the S–Br vibration.[22] The vibration of $CS_2Br_3^+$ calculated at 433 cm^{-1} and observed between 365 and 427 cm^{-1} was assigned to the out of plane deformation of the $BrCS_2$ core. This mode appears in the $(MeS)_2CSH^+$ cation at about 465 cm^{-1}.[5]

Table 3. Experimental and calculated frequencies of the cation of **1** (for the full list of experimental and calculated vibrations of the anion and cation of **1** see Table C in the Supporting Information).

Experiment		MP2/TZVPP		BP/SVP		Possible
ν [cm^{-1}]	intensity	ν [cm^{-1}]	intensity [km mol^{-1}]	ν [cm^{-1}]	intensity [km mol^{-1}]	assignment
		86	(0)	79	(0)	
		91	(1)	81	vw (1)	
		100	(0)	88	(0)	
		117	(1)	106	vw (1)	
		188	(0)	176	(0)	
257	w	264	(1)	247	vw (2)	δ(S–C–Br)
365	[a]	430	w (21)	377	vw (11)	δ($BrCS_2$)
	[a]	433	vw (3)	402	vw (3)	γ($BrCS_2$)
–427	[a]	468	w (31)	409	w (43)	ν(S–$Br_{1/4}$)
492	w	512	vw (18)	466	vw (13)	ν(S–$Br_{2/5}$)
916	w	956	w (70)	894	w (48)	ν(C–Br)
973	[a]	1057	w (217)	960	w (85)	ν_{as}(S–C–S)

[a] Approximate position of the $CS_2Br_3^+$ bands overlapping with anion bands.

Discussion

On the mechanism of the formation of 1: There is no doubt that the solvent CS_2 takes part in the reaction leading to **1** so that we now write the following incomplete reaction in Equation (1):

$$\begin{aligned} &AsBr_3 + Br_2 + Ag[Al(OR)_4] + CS_2 \rightarrow \\ &CS_2Br_3^+[Al(OR)_4]^- + AgBr + \ldots \end{aligned} \tag{1}$$

To investigate how and which species reacted with CS_2 we carried out ab initio calculations at the MP2/TZVPP level, including the estimation of the Gibbs energy of the reactions at 298 K in CH_2Cl_2 (COSMO solvation model). The state of the participating particles is either in CH_2Cl_2 as indicated by subscript "(CH_2Cl_2)" or solid as indicated by subscript "(s)". We assumed that in the first step of the reaction, the $AsBr_4^+$ ion was formed from $AsBr_3$, Br_2 and the silver salt [Eq. 2)]:

$$\begin{aligned} &AsBr_{3\,(CH_2Cl_2)} + Br_{2\,(CH_2Cl_2)} + Ag^+{}_{(CH_2Cl_2)} \rightarrow \\ &AsBr^+_{4\,(CH_2Cl_2)} + AgBr_{(s)} \quad \Delta G^o = -255\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{2}$$

The pentavalent arsenic atom in $AsBr_4^+$ may than serve as an oxidant for CS_2 in the following 4e^- oxidation reaction [Eq. (3)]:

$$\begin{aligned} &AsBr^+_{4\,(CH_2Cl_2)} + CS_{2\,(CH_2Cl_2)} \rightarrow \\ &CS_2Br^+_{3\,(CH_2Cl_2)} + {}^1\!/_6 As_6Br_{6\,(s)} \quad \Delta G^o = -56\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{3}$$

forming an As^I-bromide that could be oligomeric, that is, As_6Br_6, see Supporting Information. The entire reaction is exergonic by –311 kJ mol^{-1} [Eq. (4)]:

$$\begin{aligned} &AsBr_{3\,(CH_2Cl_2)} + Br_{2\,(CH_2Cl_2)} + Ag^+{}_{(CH_2Cl_2)} + CS_{2\,(CH_2Cl_2)} \rightarrow \\ &CsBr^+_{3\,(CH_2Cl_2)} + AgBr_{(s)} + {}^1\!/_6 As_6Br_{6\,(s)} \\ &\Delta G^o = -311\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{4}$$

To confirm this hypothesis we reacted pure $AsBr_4^+$ $[Al(OR)_4]^-$ in CH_2Cl_2 with excess CS_2 at –50 °C, allowed the mixture to warm to room temperature and removed all the volatiles in vacuo. The residue was dissolved in CD_2Cl_2 and the ^{13}C NMR spectrum was identical to that of crystals of **1**.[34] It should be mentioned that in the presence of excess carbon disulfide the carbocation signal could not be detected presumably due to exchange processes in the solution even at low temperatures. We also calculated a different route, which excludes the participation of $AsBr_3$ in the reaction assuming that only Ag^+, Br_2, and CS_2 are necessary to form **1** in the following reaction [Eq. (5)]:

$$\begin{aligned} &Ag^+{}_{(CH_2Cl_2)} + 2\,Br_{2\,(CH_2Cl_2)} + CS_{2\,(CH_2Cl_2)} \rightarrow \\ &CS_2Br^+_{3\,(CH_2Cl_2)} + AgBr_{(s)} \quad \Delta G^o = -226\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{5}$$

Since the reaction in Equation (5) is exergonic, we conducted an experiment in which Br_2 was condensed into a cooled solution of $Ag[Al(OR)_4]$ in CH_2Cl_2/CS_2 1:1. Immediate precipitation of AgBr was observed. From this reaction yellow crystals were obtained in 38 % yield that proved to be **1** (NMR, IR spectroscopy). This demonstrates that **1** may also be obtained by a reaction according to Equation (5) and one cannot distinguish between routes in Equations (4) and (5).

Structure and bonding of $CS_2Br_3^+$: The experimentally approximated charge of the sulfur atoms together with the careful analysis of the number and strengths of the fluorine contacts to the C, Br, S atoms of the cation and the population analysis of $CS_2Br_3^+$ indicate a delocalized bonding situation (see resonance structures in Figure 4).

Structure A has practically no contribution, since only one very weak fluorine contact (3.183 Å av) to the carbenium center is present. The most important structures are B, C, and D in which the majority of the charge resides on the S and (C–)Br atoms. Consequently the C–S and C–Br bonds are shortened by about 0.07 to 0.09 Å relative to a C_{sp^2}–S single bond length[29,12] (Table 4) and 0.07 Å (av) if compared with $d(C_{sp^2}–Br)$[29] (Table 4). This suggests strong double bond contributions to both, the C–S and C–Br bonds.

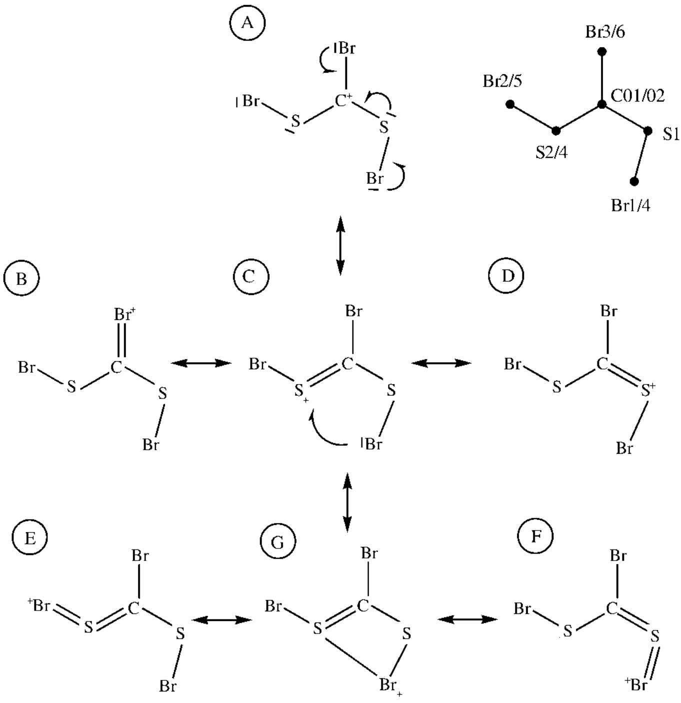
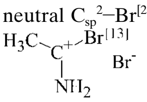
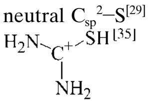
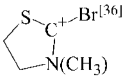
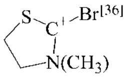
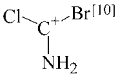


Figure 4. Delocalization of the carbenium charge in the $CS_2Br_3^+$ ion by seven likely mesomeric resonance structures A–G.

Table 4. C_{sp^2}–Br and C_{sp^2}–S distances in carbocations and in neutral molecules.

Compound	d(C–Br) [Å]	Compound	d(C–S) [Å]
neutral $C_{sp}{}^2$–Br[29]	1.881 to 1.889	neutral $C_{sp}{}^2$–S[29]	1.751 to 1.773
 $H_3C-C^+(Br)(NH_2)\ Br^-$ [13]	1.90	 $H_2N-C^+(SH)(NH_2)$ [35]	1.739
 [36]	1.849(9)	 [36]	1.694(10)
 $Cl-C^+(Br)(NH_2)$ [10]	1.843(9)	$C(SH)_3{}^+$[7]	1.683(5) to 1.712(6)
$CS_2Br_3{}^+$	1.818(3)	$CS_2Br_3{}^+$	1.671(3),[b] 1.699(3)[b]
$CBr_3{}^+$[20]	1.806(16)[a]	$Ar^1C(=S)Ar^2$[12]	1.611(5)

[a] Average value calculated from 1.783(16), 1.787(16) and 1.851(16) distances. [b] Average values of equivalent C–S bonds.

The range of the C–Br bond lengths given in Table 4 is in good agreement with the theoretical prediction of the π-donating strength of the ligands: with the electron-rich NH_2 group[35,36] as electron donor the cations are clearly iminium salts; however, $CS_2Br_3{}^+$ is a mixture between sulfonium and bromonium, while $CBr_3{}^+$ is clearly a bromonium cation and not a carbenium ion. The similarity of the C–Br distances in $CS_2Br_3{}^+$ and $CBr_3{}^+$ ions confirm the similar bonding situation as a result of the similar electronic properties of the SBr and Br ligands (see also π MOs below). The structures E, F, and G play a smaller, but still relevant role. The S–Br distances in the structure are slightly shortened and many weak fluorine contacts are formed to the (S–)Br atoms, indicating the presence of a small positive partial charge on these (S–)Br moieties. The charge residing on the equivalent sets of Br1, Br4 atoms and Br2, Br5 atoms is different, since Br1 and Br4 exhibit nine contacts, while for Br2 and Br5 only five contacts are observed. An explanation for this behavior may be found in structure G in Figure 4: The contacts Br1–S2 and Br4–S4 are short, 3.083(3) Å and 3.122(3) Å respectively (sum of the van der Waals Radii of S and Br: 3.70 Å), so the bromine atoms can also serve as electron donors for the sulfur atom in the second S–Br moiety. This also explains the different C–S distances (1.671(3) Å and 1.699(3) Å, on average): C01–S2 and C02–S4 are shortened as a result of the additional C=S bond in resonance structure G so that the set of equivalent C01–S2 and C02–S4 bonds have more π character than the other C–S bonds.[37] This assignment is in good agreement with the lower estimated partial charges residing on the sulfur atoms S2 and S4 (Table 2). As a result of the electron donation from the bromine to the sulfur atom, the partial charge on S2/S4 is reduced to +0.23, while on S1/S3 it is +0.30. The $CS_2Br_3{}^+$ ion forms a planar 10π-system. The six relevant π orbitals (five occupied and one unoccupied, HF/TZVPP level) are shown in Figure 5 as a projection along its C_s mirror plane.

The most important noncancelled π MO in Figure 5 is HOMO−4. This orbital delocalizes a π bond over the central CS_2Br region. In contrast the S–Br π bonds in HOMO−2 and HOMO−3 are cancelled by the HOMO and HOMO−1. This again underlines our conclusion that the SBr moieties are electronically close to the Br atom and, therefore, the 10π $CS_2Br_3{}^+$ ion is closely related to the 6π $CBr_3{}^+$ ion with very similar MOs to HOMO−4 and LUMO.

Four electron oxidation of CS_2: The reaction $AsBr_4{}^+ + CS_2 \rightarrow CS_2Br_3{}^+ + {}^1\!/_6 As_6Br_6$ is a rare example of an electrophilic four-electron oxidation reaction. To our knowledge this is the first report of an electrophilic oxidation of CS_2 by a cation. The only related example we found is the radical oxidation of CS_2 with gaseous Cl_2 leading to $Cl_2C(SCl)_2$,[38] which could be considered as a precursor of the analogous carbocation $CS_2Cl_3{}^+$. All other reactions involve nucleophilic attack on carbon disulfide as a first step and then further reactions. The respective neutral bromo compound $Br_2C(SBr)_2$ is unknown.

Conclusion

We have synthesized and structurally characterized the first carbocation that incorporates a S–X bond (X = halogen) directly attached to the carbenium center. We showed that there are two possible ways to synthesize the $CS_2Br_3{}^+$ cation: 1) by $4e^-$ oxidation of CS_2 with $AsBr_4{}^+$ and 2) by a combination of Ag^+, $2Br_2$, and CS_2. The $CS_2Br_3{}^+$ ion represents a 10π electron system in which the positive charge is

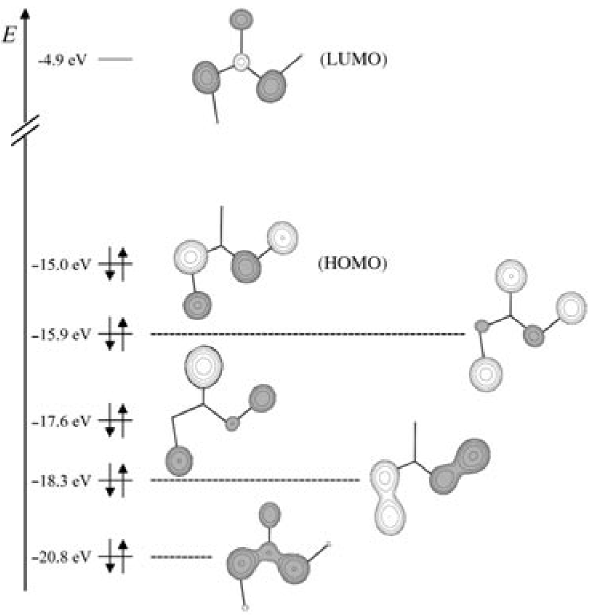


Figure 5. The six π MO's of the $CS_2Br_3^+$ ion with their energies in eV shown as a projection along the mirror plane of the cation (HF/TZVPP level).

mainly delocalized over the (C−)Br and S atoms. The electronic properties of the S−Br moieties are close to those of isolated Br atoms. Therefore, $CS_2Br_3^+$ is electronically very similar to the CBr_3^+ ion with analogous π MOs at the CS_2Br core. Equation (3) is a rare example of a $4e^-$ oxidation reaction among main group elements. The $AsBr_4^+$ ion appears to be a selective oxidant, which may further be applied in synthesis. Experiments in this direction are in progress.

Experimental Section

All manipulations were performed by using standard Schlenk or dry box techniques and a nitrogen or argon atmosphere (H_2O and O_2 < 1 ppm). Apparatus were closed by J. Young valves. All solvents were rigorously dried over P_2O_5 and degassed prior to use and stored under N_2. $AsBr_3$ was prepared from arsenic trioxide, sulphur, and bromine according to the method described in the literature[39] and its purity was checked by Raman spectroscopy. The silver aluminate $Ag[Al(OR)_4]$ was prepared according to the literature.[31] Raman and IR spectra were recorded using a 1064 nm laser on a Bruker IFS 66v spectrometer equipped with the Raman modul FRA106. IR spectra were recorded in Nujol mull between CsI plates. NMR spectra (Bruker AC250) of sealed samples were run in CD_2Cl_2 and were referenced towards the solvent (^1H, ^{13}C) and external aqueous $AlCl_3$ (^{27}Al).

Reactions leading to $CS_2Br_3^+[Al(OR)_4]^-$:

Reaction 1 (preparation in the course of the planned synthesis of $AsBr_4^+[Al(OR)_4]^-$): $(CH_2Cl_2)Ag[Al(OR)_4]$ (1.022 g, 0.881 mmol) was weighed into a two bulbed vessel. $AsBr_3$ (0.277 g, 0.881 mmol) was dissolved in CS_2/CH_2Cl_2 (1:1, ca. 15 mL) and was added to the silver salt at −78 °C; finally Br_2 (0.141 g, 0.881 mmol, 0.045 mL) was condensed into the mixture at −196 °C. After warming the reaction mixture to about −20 °C, a colorless solid precipitated (AgBr). The solution was filtered and its volume concentrated to about one half. Both a microcrystalline solid and several single crystals of **1** precipitated at −80 °C and were isolated [0.643 g, 57 % calculated for Eq. (4)]. ^{13}C NMR (63 MHz, CD_2Cl_2, −60 °C): $\delta =$ 209.7, (s, C_{carb}), 120.5 (q, $J_{CF} = 292.1$ Hz, CF_3), 78.0 ppm (br, C_{tert}); ^{27}Al NMR (78 MHz, CD_2Cl_2, −50 °C): $\delta = 38.2$ (s, $\nu_{1/2} = 10$ Hz).

Reaction 2 [NMR tube reaction according to Eq. (3)]: $AsBr_4^+[Al(OR)_4]^-$ (0.115 g, 0.084 mmol) was weighed into a NMR tube glass-blown onto a valve. CH_2Cl_2 (ca. 1.0 mL) and CS_2 (ca. 0.3 mL) were transferred to the tube at −30 °C, shaken a few times at room temperature and stored over night at −30 °C. A slightly gray solid precipitated (As_6Br_6?). The solvent was removed under vacuum and replaced by CD_2Cl_2. The ^{13}C NMR spectra of this sample at −30 °C showed only the $CS_2Br_3^+$ signal at $\delta =$ 210.3 ppm in addition to the anion signals at $\delta = 121.0$ (q, $J_{CF} = 292.5$ Hz, CF_3) and 78.2 ppm (br, C_{tert}).

Reaction 3 [between the silver salt, dibromine, and carbon disulfide according to Eq. (5)]: $Ag[Al(OR)_4]$ (0.998 g, 0.93 mmol) was weighed into a two bulbed vessel, dissolved in CH_2Cl_2 (15 mL) and cooled to −78 °C. An excess of CS_2 (approximately 3 mL), followed by Br_2 (0.297 g, 1.86 mmol, 0.1 mL) was condensed into the solution, and the reaction mixture was warmed to −30 °C and occasionally shaken. The off white precipitate was filtered off from the dark brown solution after a few hours, and the concentrated filtrate was stored at −30 °C forming yellow crystals (yield 0.415 g, 38 %). ^{13}C NMR (63 MHz, CD_2Cl_2, −30 °C): $\delta = 210.3$ (s, C_{carb}), 121.0 (q, $J_{CF} = 292.9$ Hz, CF_3), 78.2 (br, C_{tert}).

Computational details: All computations were done with the program TURBOMOLE.[40] The geometries of all species were optimized at the (RI-)MP2 level[41] with the triple ζ valence polarization (two d and one f functions) TZVPP basis set.[42] The 28 core electrons of Ag were replaced by a quasi-relativistic effective core potential.[43] All species were also fully optimized at the BP86/SV(P) (DFT) level, albeit these geometries are not shown. Approximate solvation energies (CH_2Cl_2 with $\varepsilon_r = 8.93$) were calculated with the COSMO model[44] at the BP86/SV(P) (DFT) level using the MP2/TZVPP geometries. Frequency calculations were performed for all species and structures represent true minima without imaginary frequencies on the respective hypersurface (with the exception of two $CS_2Br_3^+$ isomers). For thermodynamic calculations the zero-point energy and thermal contributions to the enthalpy and the free energy at 298 K were included.[45] The calculation of the thermal contributions to the enthalpy and entropic contributions to the free energy were done with Gaussian 98W.[46] For all species a modified Roby–Davidson population analysis based on occupation numbers (paboon) has been performed using the (RI-)MP2/TZVPP electron density. The HF/MP2TZVPP molecular orbitals (Figure 5) were created with the MOLDEN 3.7 software.[47]

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[27] This shows most strongly for CI_4 and CI_3^+ which resonate at $\delta = -292$ and $+97$ ppm and thus far from where they are expected without relativistic contribution.

[28] Crystal structure determination of $CS_2Br_3^+[Al(OC(CF_3)_3)_4]^-$: IPDS (Stoe), graphite monochromated $Mo_{K\alpha}$ radiation (0.71073 Å), $T = 100(2)$ K, unit cell determination: 2000 reflections, corrections: Lorentz, polarization and numerical absorption correction, min/max transmision = 0.3802/0.6675; $\mu = 3.899\,cm^{-1}$, direct methods with SHELXS-97, refinement against F^2 with SHELXL-97. Space group: $P2_1/c$, $Z = 8$, $a = 24.081(5)$ Å, $b = 15.359(3)$, $c = 18.851(4)$ Å, $\beta = 99.90(3)°$; $V = 6868(2)$ Å^3, $\rho_{calcd} = 2.481\,g\,cm^{-1}$, $2\theta_{max.} = 51.2°$, reflections: 42392 collected, 12809 unique ($R_{int} = 0.0617$), 9049 observed (2σ), 1281 parameters, 48 restraints, $R1 = 0.0445$, $wR2 = 0.0787$, $R1$ (all data) = 0.0776, $wR2$ (all data) = 0.0882, GooF = 1.005, restrained GooF = 1.026. Bromine and sulfur atoms of both the cations had to be split over two positions and were included in the refinement with occupation factors of 11 to 14% for the disordered positions. The six (-CF_3) groups of the anion (#2) had to be split over two positions and the disordered atoms were included isotropically in the refinement. Their position was fixed with restraints (SADI command). All other atoms were refined anisotropically. CCDC-228671 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[32] The Al−O bond lengths of the anion for Al1−O vary slightly from 1.716(2) to 1.724(2) Å, average 1.719 Å; for Al2−O ranges from 1.718 to 1.730–1.724 Å on average. Both anions are comparable and similar to the published Al−O distance of 1.725 Å.[31] The Al−O−C angles have typical values[31] for the $Al[OR]_4^-$ ion: range 145.29(19)°–149.4(2)°, 148.4(2)° (#1) and 147.2(2)° (#2) on average.

[33] The contacts s (in valency units v.u.) have been defined as $s = (R/R_0)^{-N}$, in which R is the observed distance, R_0 is the covalent bond distance (bond order = 1) of the bond in question and N is a empirically derived constant. For S···F contacts $N = 3.8$ and $R_0 = 1.55$ Å. see: I. D. Brown, in *Structure and Bonding in Crystals, Vol. 2* (Eds.: M. O'Keefe, A. Navrotsky), Academic Press, London, **1981**, p. 1.

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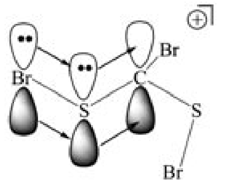
[37] The bonding in the $CS_2Br_3^+$ ion along the C−S−Br unit can be described as a 4e-3c bond. The three π orbitals, two occupied lone pair orbitals of Br and S (4e), and one unoccupied p_z orbital residing at the carbenium center are involved resulting in delocalized MOs (see below). The π electrons of the Br atom are pushed towards the carbenium center, rather than donated into one of the d orbitals of the sulphur atom. This is shown in Figure 4 as resonance structure E and F including two double bonds around the S atom (a $Br^+{=}S{=}C$ moiety); this formulation does not imply the use of sulfur d orbitals as acceptors to form the two double bonds, but uses only p-type atomic orbitals at Br, S and C (see below). By this interaction, electron density is removed from the occupied sulfur lone-pair orbital into the empty p_z orbital at the carbenium center. The electron deficiency at S can then be removed in part by a further donation of electrons from the Br lone pair orbital to the (now only partially filled) S lone pair orbital. A similar interaction is responsible for resonance structure G, for which also no sulfur d orbital participation has to be assumed.



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