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Chlorine Back-Donation in the Crystal Structure of a Chloro-Substituted Carbocation

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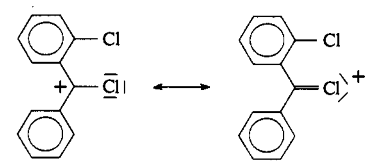
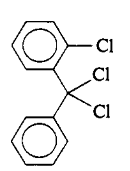
Abstract: The first crystal structure analysis of the salt of a chloro-substituted carbocation with a short C^+–Cl bond of 1.668(8) Å, i.e., a significant shortening of 0.066(8) Å if compared with the C_{sp^2}-Cl reference value of 1.734(2) Å from the Cambridge File, has been determined (**1**·SbF_6). The shortening points to a partial double bond character ($C{=}Cl^+$) and thus supports the results of Olah (NMR spectroscopy), Vančik and Sunko (IR spectroscopy), and Schaefer and Reynolds (ab initio calculations) about the chlorine back-donation in carbocations of this type.

The stabilization of chloro-substituted carbocations has been recently examined experimentally by Olah[1] (NMR spectroscopy) and by Vančik and Sunko[2] (IR spectroscopy) and theoretically by Schaefer[3] and Reynolds[4] (ab initio calculations). We report here on the first crystal structure analysis of the salt of a chloro-substituted carbocation with a significant C^+–Cl bond shortening (**1**·SbF_6) indicating a partial double bond character ($C{=}Cl^+$), which we interpret as the result of chlorine back-donation.



1 **1'**



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Results

The preparation of stable crystalline salts of chloro-substituted carbocations has been described by Volz[5] and Olah[6] many years ago, but up to date, no crystal structure of such a salt has been obtained which shows the expected C^+–Cl shortening.[7,9] After several unsuccessful attempts,[10] we prepared crystals of **1**·SbF_6 by reaction of **2**[12] with $AgSbF_6$ and subsequent recrystallization. The resulting structure is shown in Figure 1; some selected parameters are given in Figure 2.

The planar cationic carbon atom C1 is bonded to the two slightly twisted phenyl rings (Cl1–C1–C11–C12 −41(1)°, Cl1–C1–C21–C22 −16(1)°) and the chlorine atom Cl1 and is surrounded by two fluorine atoms of counterions with distances slightly larger than the sum of the van der Waals radii of C and F (3.17 Å; C1⋯F1′ 3.228(9) Å, C1⋯F3 3.455(9) Å). The C^+–C_{ipso} bonds (C1–C11 1.432(9) [1.437] and C1–C21 1.42(1) [1.43] Å) have lengths similar to those in the unsubstituted trityl cation[13] (average 1.449(2) Å). Although our structure is not very precise, the C–C bond lengths in the two phenyl rings of **1** show a pattern similar to those in the trityl cation: ignoring the chlorine at C12, the average C_{ipso}–C_{ortho} bond of **1** (1.416(6) Å) is slightly longer than the C_{ortho}–C_{meta} (1.370(4) Å) and the C_{meta}–C_{para} (1.39(1) Å) bonds (trityl cation:[14] 1.416(6), 1.384(6), 1.393(9) Å).

The two C_{sp^2}–Cl bonds have significantly different lengths: C1–Cl1 1.668(8) [1.677] Å and C12–Cl2 1.726(9) [1.737] Å. While C12–Cl2 is similar to the C_{ar}–Cl reference value[8] of 1.739(1) Å, C1–Cl1 is significantly shortened by 0.066(8) [0.057] Å if compared with the C_{sp^2}–Cl reference value[8] of 1.734(2) Å.

Discussion

The phenyl rings in **1** seem to stabilize the cation by charge delocalization into the ring π systems similar to those of the trityl cation, where comparable C–C bond lengths and also a red color are observed. Because the experimental determination of the structure of a chloro-substituted carbocation is (with the exception of a highly stabilized ion[7]) without precedent, the C^+–Cl bond needs to be discussed in detail. Two major factors may influence the length of a (nonbridging) carbon–chlorine bond in a carbocation: the hybridization of the C orbital involved in the σ_{C-Cl} bond and a possible π_{C-Cl} bond resulting from an interaction of a filled Cl 3p orbital with the empty C 2p orbital ("back-donation"). Because one can calculate the individual orbital hybridizations of a trigonal C atom from the bond angles according to Haddon[15] and because the empirical relationship between the thus computed hybridizations and the C–Cl bond length in σ_{C-Cl} bonds is known[16-18] (see Figure 3), one can estimate the lengths

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(6) Olah, G. A.; Svoboda, J. J. *Synthesis* **1972**, 307–308.

(7) The crystal structure of the chlorobis(dimethylamino)carbenium ion has a C^+–Cl bond length of 1.724(6) Å (Chuklanova, E. B.; Gusev, A. I.; Zhdanov, A. S.; Belyakova, Z. V.; Chevchenko, V. M.; Sheludyakov, V. D. *Koord. Khim.* **1987**, *13*, 1109–1112), which does not deviate significantly from the average length of a C_{sp^2}–Cl bond (1.734(2) Å).[8]

(8) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. In *International Tables of Crystallography, Volume C*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; pp 685–706.

(9) The crystal structure of the 2,4,4-trifluoro-1,3-dithietan-2-ylium ion (Antel, J.; Harms, K.; Jones, P. G.; Mews, R.; Sheldrick, G. M.; Waterfeld, A. *Chem. Ber.* **1985**, *118*, 5006–5008) has a shortened C^+–F bond (1.25(1) Å; reference value[8] C_{sp^2}–F 1.340(2) Å), but the C_{sp^3}–F bonds of this molecule are also shortened (1.294(7) Å; reference value[8] 1.351(2) Å). Correction for thermal motion would lengthen all C–F bonds by ca. 0.05 Å and thus yield an overall C^+–F shortening of ca. 0.04 Å.

(10) The following salts $RR'C–Cl^+ A^-$ have been prepared, which were not suitable for a crystal structure analysis: $R = R' = C_6H_5$ and $A = SbF_6$, $SbCl_6$, AsF_6, BF_4; $R = C_6H_5$, $R' = Cl$, and $A = SbF_6$, $SbCl_6$; $R = C_6H_5$, $R' = C_6F_5$, and $A = SbF_6$, $SbCl_6$; $R = C_6H_5$, $R' = 3\text{-}CH_3C_6H_4$, and $A = SbCl_6$; $R = C_6H_5$, $R' = 4\text{-}C_6H_5C_6H_4$, and $A = SbF_6$, $SbCl_6$. Upon addition of SbF_5 to a large excess of $CFCl_3$ at −20 °C under argon, a colorless precipitate is formed, which may be $CCl_3{}^+SbF_6{}^-$. The dry powder becomes brown after a few minutes at room temperature. Recrystallization from CH_2Cl_2 leads to decomposition; from a SO_2 solution, only crystalline SO_2·SbF_5 could be obtained.[11]

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(13) (a) Gomes de Mesquita, A. H.; MacGillavry, C. H.; Eriks, K. *Acta Crystallogr.* **1965**, *18*, 437–443. (b) Krebs, B.; Paulat, V. *Z. Naturforsch.* **1979**, *34B*, 900–905. (c) Calderazzo, F.; Pallavicini, P.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1990**, 2743–2746. (d) Krausse, J.; Heublein, G.; Rudakoff, G.; Leibnitz, P.; Reck, G. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 45–49.

(14) Averages of corresponding bonds of the trityl cations in ref 13a,b, and d. The cation from ref 13c has been omitted here because all phenyl rings were constrainted to regular hexagons.

(15) Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837–2842.

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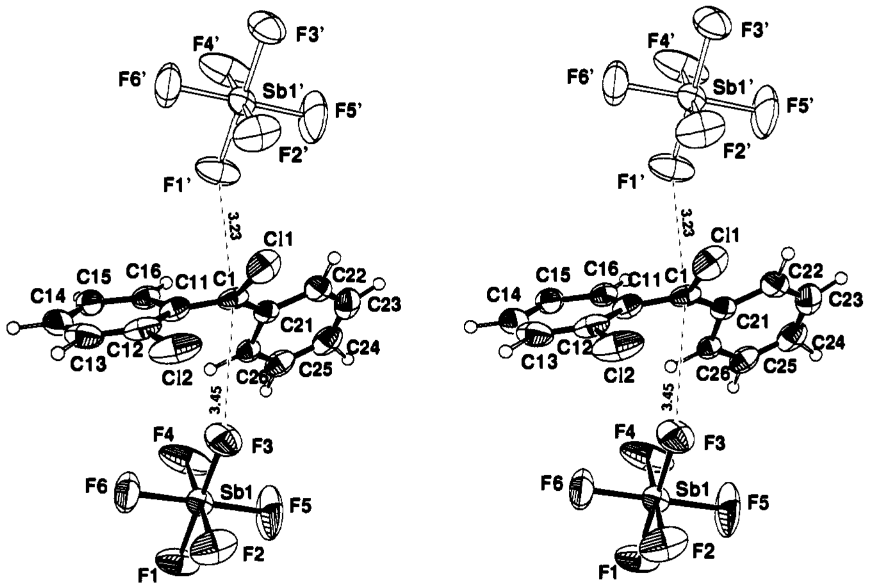

Figure 1. Stereo drawing[22,23] of the crystal structure of 1·SbF_6. The atoms of the symmetry-related ($x + 1, y + 1, z$) anion are drawn as white ellipsoids and have primed labels. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å. Distances are given in angstroms.

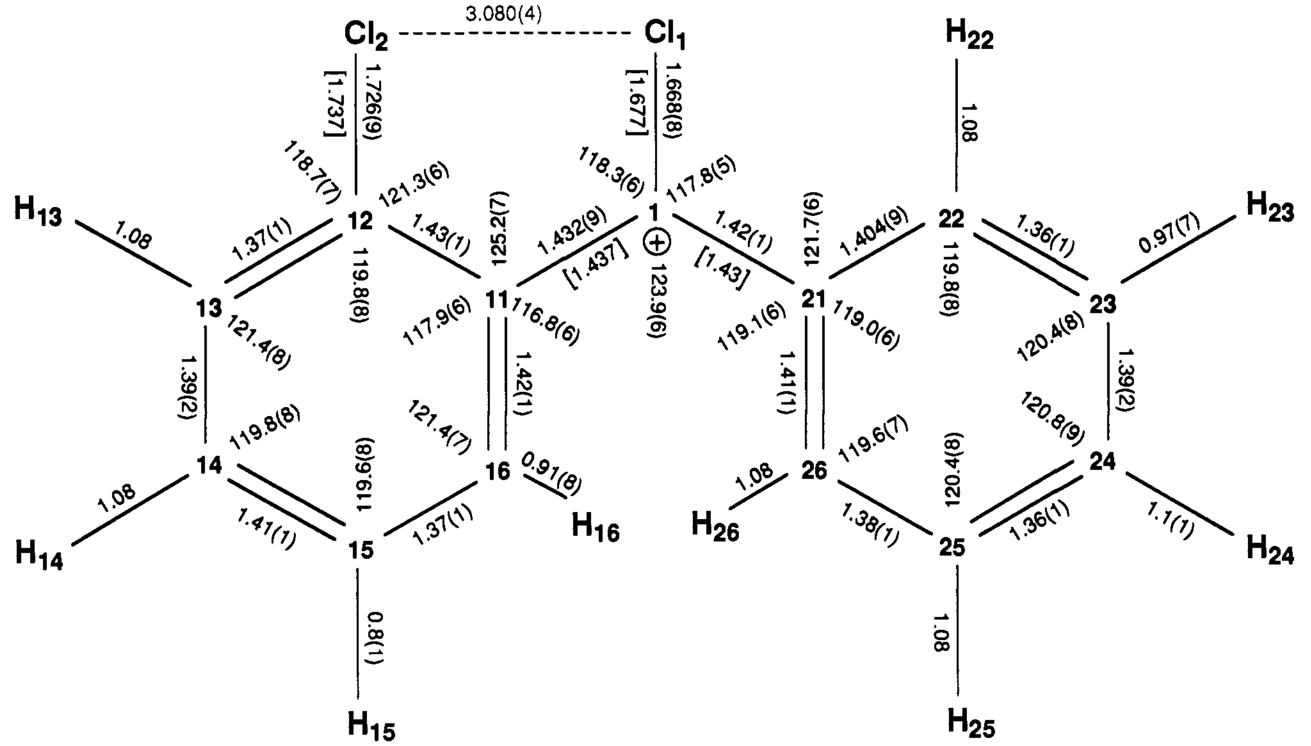

Figure 2. Bond lengths (angstroms; in brackets: corrected for libration) and angles (°) in the crystal structure of **1**.

of the two C–Cl bonds in **1** assuming pure σ_{C-Cl} bonds.

For C1–Cl1, one obtains with Haddons method[15] a C hybrid orbital of the type $sp^{2.53}$ and for C12–Cl2 a C hybrid orbital of the type $sp^{1.99}$. From the empirical hybridization–length relationship and its 99.9% prognosis intervals drawn in Figure 3, one would expect the C1–Cl1 length with 99.9% probability to be in the interval [1.70 Å, 1.80 Å] and the C12–Cl2 length in the interval [1.67 Å, 1.76 Å]. While the C12–Cl2 bond lies within the predicted range, the C1–Cl1 bond must be considered as an outlier. Our explanation is that C1–Cl1 contains a partial π bond, which shortens the interatomic distance. The existence of such a partial π bond has also been inferred from NMR chemical shift[1] and IR frequency[2] data and from ab initio studies[3,4] of halogen-substituted carbocations. We cannot exclude the possibility that some shortening also arises from inductive effects in the σ_{C-Cl} bond, but partial π bonds have also been observed in the crystal structures of sulphur- and selenium-substituted carbocations,[19] where C^+-XCH_3 (X: S, Se) shortenings of about 0.15 Å, planar conformations, and hindered rotations about the C^+–X bonds

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(16) Laube, T. *J. Comput. Chem.* **1988**, *9*, 356–361.

(17) The relationship in ref 16 includes C–Cl single bonds emanating from trigonal[15] and from tetrahedral[16] C atoms.

(18) Although the adjusted function has a significant quadratic term, it is not very distinct (see prognosis intervals) from a linear relationship, which was proposed by Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *11*, 96–120.

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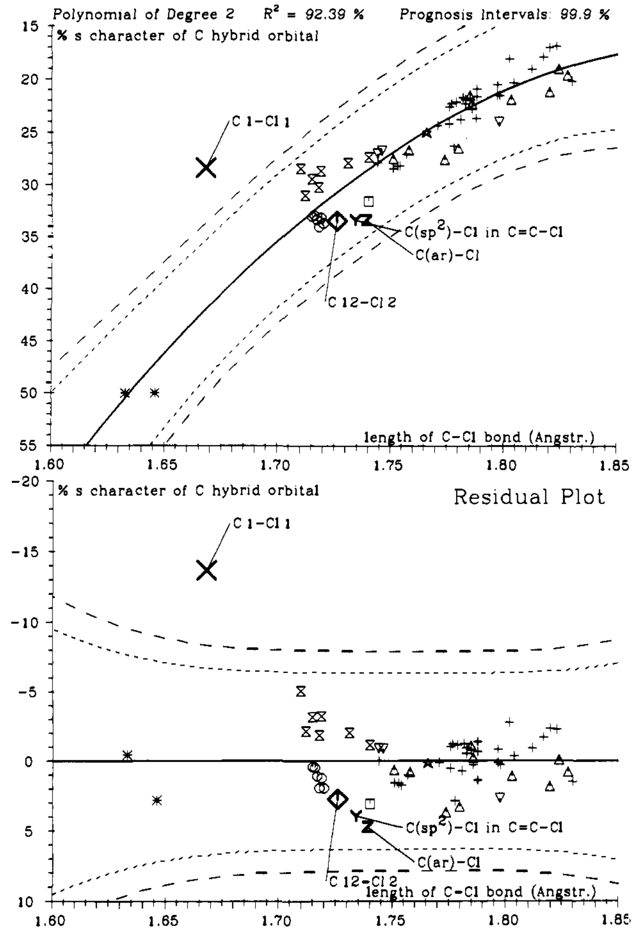

Figure 3. Top: dependence of the s character (in %) of the carbon hybrid orbital in C–Cl bonds (estimated from experimentally determined structures with the methods from refs 15 and 16) on the C–Cl bond lengths (angstroms). Bottom: corresponding residual plot. The polynomial was adjusted by the least-squares method on the data represented by thin markers (from Figure 1 in ref 16; see also there for the different marker types; the two additional stars at 50% s character represent examples with a –C≡C–Cl fragment[8]). The functions drawn with short dashes represent the individual, and those drawn with long dashes represent the simultaneous prognosis interval. The thick markers Y and Z (drawn at 33.3% s character because of lack of more precise information about the hybridization) are the reference values for C_{sp^2}–Cl and C_{ar}–Cl bonds.[8] The thick cross and square represent the C–Cl bonds of **1**.

(measured by ^{1}H NMR spectroscopy) were found.

Conclusion

The crystal structure of **1** shows an unusually short C$^+$–Cl bond, if its length is compared with suitable reference values and with an empirical C–Cl bond length–hybridization relationship. We interpret this shortening as an indication of a partial double bond character (resonance formula **1′**) resulting from chlorine back-donation in agreement with NMR,[1] IR,[2] ab initio,[3,4] and X-ray results[19] about related systems.

Experimental Part

Synthesis of 1·SbF$_6$. A solution of 1.4 mmol of AgSbF$_6$ in 10 mL of CH$_2$Cl$_2$ was slowly added to a solution of 1.4 mmol of **2** in 30 mL of 1,1,2-trichlorotrifluoroethane at –33 °C under argon. After 30 min, the solvent was removed under high vacuum (HV) at –30 °C, and 10 mL of CH$_2$Cl$_2$ was added to the red precipitate. After being stirred at –10 °C, the solution was filtered and cooled to –69 °C within 38 h. After removal of the mother liquor and drying in the HV, a suitable crystal (deeply red) was mounted in a capillary.

Crystal Structure Analysis of 1·SbF$_6$. Enraf–Nonius CAD4 diffractometer, Mo Kα radiation, graphite monochromator, measurement at –80 °C. Space group: $P\bar{1}$ (No. 2) with a = 7.073(4), b = 8.304(6), c = 13.633(8) Å, α = 99.20(5), β = 97.41(5), γ = 101.45(5)°; V = 763.9(9) Å^3, ρ_x = 2.051 g cm^{-3}; 3230 independent reflections up to θ = 32° with $I > 3\sigma_I$. After Lp and numerical absorption correction, the structure was solved with the Patterson option of SHELXS-86[20] and refined with SHELX-76[21] ($w = \sigma_F^{-2}$; H13, H14, H22, H25, H26 riding with free temperature factor; the other hydrogen atoms could be refined freely yielding reasonable positional parameters) and XTAL3.0[22] (positional parameters of H13, H14, H22, H25, H26 not refined; 220 parameters) yielding R = 0.066, R_w = 0.062. The crystallographic pictures are drawn with ORTEP,[22,23] and the thermal motion analysis of **1** was performed with THMA11.[24] Bond lengths corrected for libration are given in brackets. Figure 3 was drawn with the Erlanger Graphik System.[25] Details about the prognosis intervals are given in the supplementary material.

Note Added in Proof. A seeming C$^+$–Cl shortening due to a partial exchange of Cl1 by F (from the anion) in **1** can be excluded because the difference density is negative in that region where a possible (partially populated) F atom should be found in such a disorder case. The ^{13}C NMR spectrum of **1**·SbF$_6$ does not show a doublet which would be expected for an ion RR′C$^+$ – F.

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Supplementary Material Available: Crystal packing diagram, tables of positional and thermal parameters, bond lengths, angles, torsion angles and contact distances; results of the thermal motion analysis of **1**; data for Figure 3 (17 pages); listings of the observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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