Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

On the nature of the stabilisation of the E…π pnicogen bond in the SbCl$_3$…toluene complex

Rabindranath Lo,[a] Petr Švec,[b] Zdeňka Růžičková, [b] Aleš Růžička,[b] and Pavel Hobza*[a,c]

[a] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2,166 10 Prague 6, Czech Republic; E-mail: hobza@uochb.cas.cz

[b] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice, Czech Republic.

[c] Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

TABLE OF CONTENTS:

QM Calculations

All the structures considered in this study were optimised at the DFT-D3/BLYP/def2-TZVPP level of theory with the TURBOMOLE 6.4 suite of programs.[1] Grimme's advanced dispersion-corrected approach[2] (DFT-D3) with the def2-TZVPP basis set was chosen, as it efficiently considers the effective-core potentials for Sb atoms.[3] Frequency calculations were performed for all the geometries to characterise them as minima with no imaginary frequency. The electrostatic potentials were generated on the molecular surfaces defined by Bader et al.,[4] as the 0.001 a.u. (electrons/bohr^3) contour of the electron density. The most positive value of the potentials (the local maximum) can be characterised as well as measured on the molecular surfaces and is designated as $V_{s,max}$. In this study, the electrostatic potentials were calculated at the HF/def2-QZVP level of theory using Gaussian09[5] and Molekel4.3[6] programs. Natural bond order (NBO) analysis was performed at BLYP/def2-TZVPP level from NBO 3.1 program [7] as implemented in Gaussian 09 using the optimized geometries. Noncovalent interaction (NCI) index calculations were done using the Multiwfn program[8] and graphical representation was displayed with the VMD program.[9] The interaction energy was decomposed by using the density functional theory-based symmetry-adapted perturbation theory (DFT-SAPT). The inaccurate energies of the virtual orbitals attained from DFT method were corrected by a gradient-controlled shift procedure. To obtain the desired shift value, PBE1PBE/aug-cc-pVDZ and PBE1PBE/def2-TZVP level of theory were taken in this study. The DFT part was treated using the localized and asymptotically corrected LPBE0AC exchange correlation functional and the aug-cc-pVDZ basis set. For, Sb atom, aug-cc-pVDZ-PP basis set has been chosen. Larger basis set (e.g., aug-cc-pVTZ) has been used to take the account of energetic values, which is underestimated in the dispersion term.

Synthetic procedure

0.55 g of $SbCl_3$ was mixed together with 0.138 mL hexafluorobenzene in toluenu (ca. 5-6 mL) and ultrasonicated for 30 min. Crystals of adduct were obtained in freezer at -28°C - m. p. -23°C, yield ~ 65%.

Crystallography

The X-ray data for colorless crystals of toluene-$SbCl_3$ adduct were obtained at -28°C and measured at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN[10]. The absorption was corrected by integration methods[11]. Structure was primarily solved by direct methods (Sir92)[12] and refined by full matrix leastsquares based on F^2 (SHELXL97)[13]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors Hiso(H) =1.2Ueq(pivot atom) or of 1.5Ueq for the methyl moiety with C-H = 0.96 and 0.93 Å for methyl and hydrogen atoms in aromatic ring, respectively. CCDC Nr. 1432791.

Table S1: Crystallographic data for toluene-$SbCl_3$ adduct.

empirical formula	Cl_3Sb (C_7H_8)
crystal system	triclinic
space group	P -1
a [Å]	7.4330(6)
b [Å]	11.8310(8)
c [Å]	12.3401(14)
α [°]	75.797(7)
β [°]	83.716(8)
γ [°]	89.257(6)
Z	4
μ [mm^{-1}]	3.343
D_x [Mg m^{-3}]	2.034
cryst size [mm]	0.59 x 0.52 x 0.43
θ range [deg]	2.14 - 27.35
T_{min}, T_{max}	0.279, 0.391
no. of reflns measd	17254
no. of unique reflns, $R_{int}{}^a$	17191, 0.0959
no. of obsd reflns [$I>2\sigma(I)$]	4203
no. of params	199
S^b all data	1.185
final R^c indices [$I>2\sigma(I)$]	0.0395
wR^{2c} indices (all data)	0.1064
Δρ, max., min. [e Å^{-3}]	1.678, -2.049

[a] $R_{\text{int}} = \Sigma|F_o^2 - F_{o,\text{mean}}^2|/\Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\text{diffrs}} - N_{\text{params}})]^{½}$. [c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$.

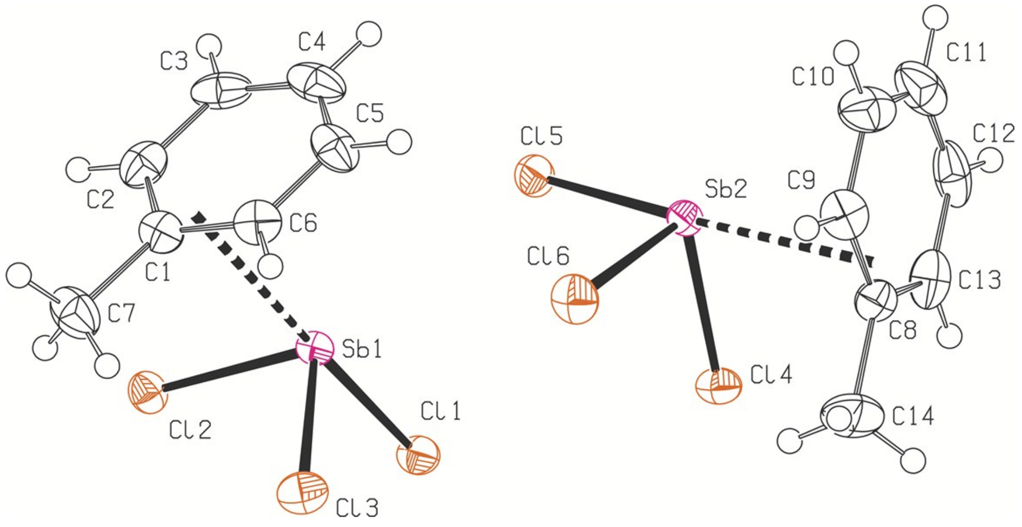

Fig. S1: Structure of toluene-$SbCl_3$ adduct - ORTEP view - 50% probability level.

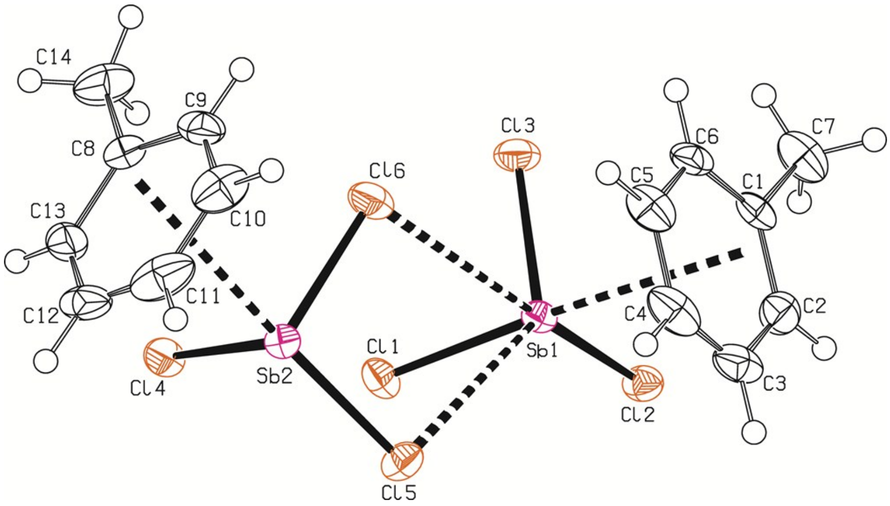

Fig. S2: Structure of toluene-$SbCl_3$ adduct - including selected intramolecular Sb-Cl short contacts - ORTEP view - 50% probability level.

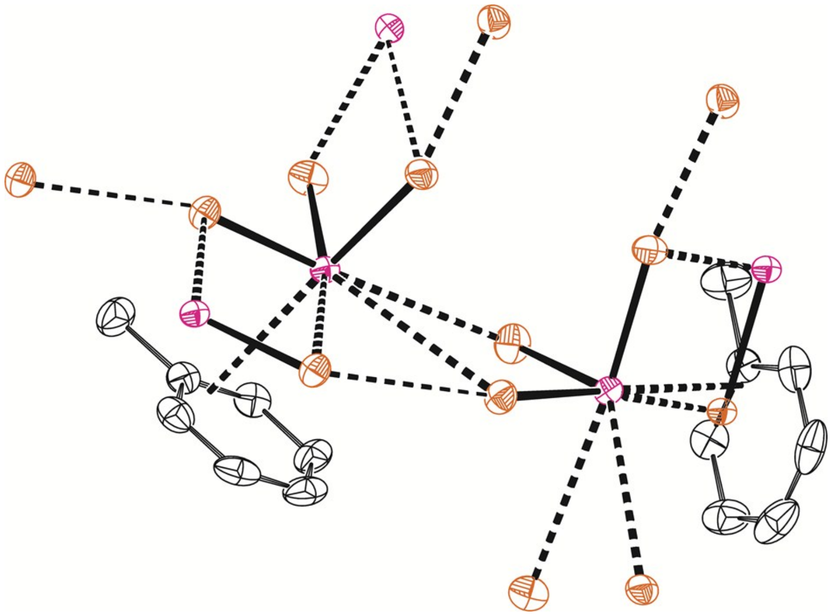

Fig. S3: Structure of toluene-SbCl$_3$ adduct - including selected intramolecular Sb-Cl and Cl-Cl short contacts - ORTEP view - 50% probability level.

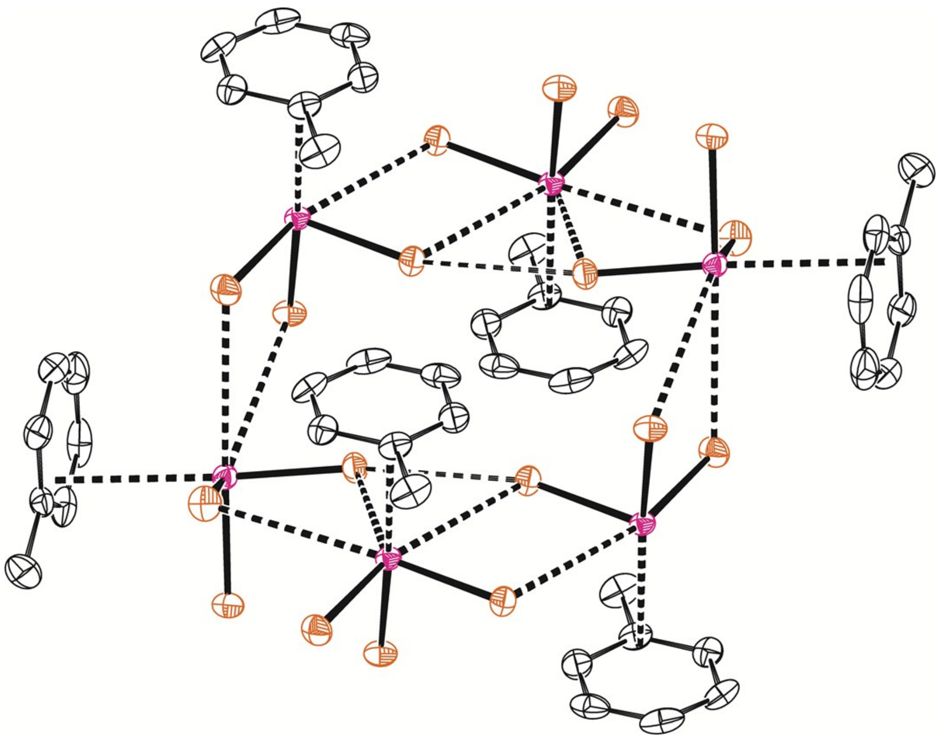

Fig. S4: Structure of toluene-SbCl$_3$ adduct - including selected intramolecular Sb-Cl and Cl-Cl short contacts - ORTEP view - 50% probability level.

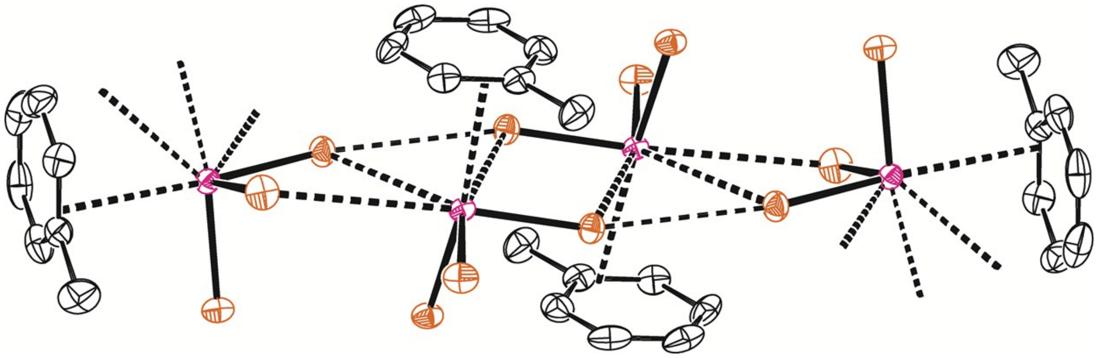

Fig. S5: Structure of toluene-$SbCl_3$ adduct - including selected intramolecular Sb-Cl and Cl-Cl short contacts - ORTEP view - 50% probability level.

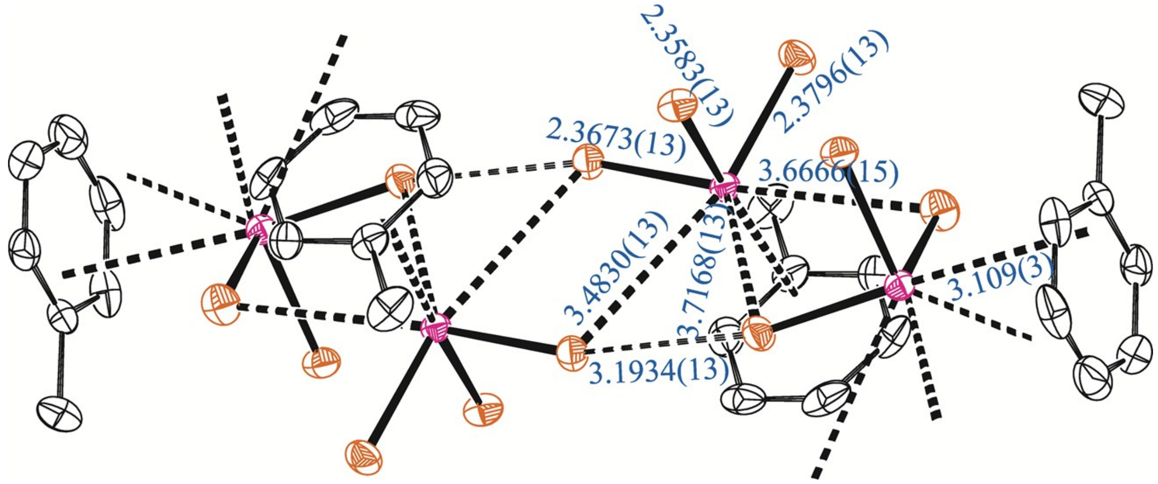

Fig. S6: Structure of toluene-$SbCl_3$ adduct - including selected intramolecular Sb-Cl and Cl-Cl short contacts and its lengths - ORTEP view - 50% probability level.

References

[1] TURBOMOLE 6.4; Universität Karlsruhe, 2012, http://www.turbomole.com

[2] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

[3] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. 2005, **7**, 3297.

[4] R. F. W. Bader, M. Carroll, J. R. Cheeseman, C. Chang, *J. Am. Chem. Soc*., 1987, **109**, 7968.

[5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. Gaussian, Inc., Wallingford CT, **2009**.

[6] a) MOLEKEL 4.3, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000-2002; b) S. Portmann, H. P. Lüthi. MOLEKEL: CHIMIA, **2007**, *28*, 555-569.

[7] NBO Version 3.1, E. D.Glendening, A. E.Reed, Eds.

[8] T. Lu, Multiwfn: A Multifunctional Wavefunction Analyzer, Version 3.0.1, Http://Multiwfn.Codeplex.Com, 2013.

[9] W. Humphrey, A. Dalke, K. Schulten, Vmd: Visual Molecular Dynamics. *J. Mol. Graphics* 1996, **14**, 33.

[10] Z. Otwinowski, W. Minor, *Methods in Enzymology* 1997, **276**, 307.

[11] P. Coppens In: F.R. Ahmed, S.R. Hall and C.P. Huber Editors, Crystallographic Computing, **1970**, pp. 255 – 270, Copenhagen, Munksgaard.

[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *Journal of Applied Crystallography* 1994, **27**, 1045.

[13] G. M. Sheldrick, SHELXL-97, University of Göttingen: Göttingen, **2008**.

Cartesian coordinates of optimized geometries

2b

Sb	3.572569996	7.483531660	1.876876436
Cl	2.015483777	5.900334262	0.957742597
Cl	2.238583001	8.213475207	3.740506611
Cl	3.100006280	9.318030194	0.394241854
C	4.236365112	4.808701174	4.040805778
C	4.875424194	4.227833652	2.928714420
C	4.938177038	5.789987238	4.770044377
C	6.234958032	6.172389536	4.404978420
C	2.842829557	4.387025405	4.457616050
C	6.858326893	5.581969860	3.296739589
C	6.173098040	4.608221310	2.559287017
H	4.346087386	3.478706953	2.342587895
H	4.455608098	6.264129584	5.622955003
H	6.756052936	6.933482973	4.982784547
H	2.324833613	3.860146786	3.649527049
H	2.236233508	5.255677655	4.740298814
H	2.885224507	3.716547410	5.327237172
H	7.865043468	5.879536046	3.010607311
H	6.645004567	4.145653097	1.694399059

2C

C	-1.185292576	-1.356849199	2.257533571
C	-1.192173524	0.010670590	2.569659508
C	0.007999823	0.726294534	2.719905694
C	1.222109179	0.032563714	2.547373671
C	1.236410937	-1.331481645	2.236248039
C	0.029710365	-2.033400259	2.087937208
Sb	-0.109136704	-0.606951309	-1.120242995
Cl	0.054487943	0.505356567	-3.248828719
Cl	1.333257727	-2.467179597	-1.601104379
Cl	-2.216698466	-1.704843842	-1.471106884
C	0.009528593	2.201680079	3.065611617
H	2.163832125	0.569321899	2.658312746
H	2.184163850	-1.847269419	2.097245499
H	0.038825293	-3.091115860	1.835919798
H	-2.126123346	-1.888398951	2.134321387

H	-2.142880656	0.526665406	2.696591397
H	-1.007142341	2.607295201	3.111178070
H	0.573431761	2.783262104	2.324238651
H	0.485690016	2.375379986	4.040206123

2d

C	-0.030723024	2.282194591	8.735149653
C	0.691622001	1.260504646	8.100268267
C	1.031946387	1.380295913	6.744685467
C	0.648908038	2.521199417	6.024011423
C	-0.074130324	3.540401500	6.658406998
C	-0.413965291	3.421053924	8.013906647
Sb	-2.374646065	0.158862791	6.630872994
Cl	-1.190803889	-1.320146169	5.154403247
Cl	-4.612241425	-0.422495090	5.970945470
Cl	-2.257001348	-1.174412934	8.625039488
H	1.581258272	0.582748607	6.249952913
H	0.911950557	2.612177975	4.972096423
H	-0.370527669	4.425816311	6.099388765
H	-0.974382579	4.213747534	8.505779662
H	-0.297574843	2.184985012	9.785413888
H	0.978545201	0.371115971	8.656491696