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Type of the Paper Article

Identification of the Tetrel Bonds between Halide Anions and Carbon Atom of Methyl Groups Using Electronic Criterion

Ekaterina Bartashevich [1,*], Yuriy Matveychuk [1] and Vladimir Tsirelson [1,2]

[1] South Ural State University Chelyabinsk, Russia; info@susu.ru
[2] D.I. Mendeleev University of Chemical Technology, Moscow, Russia;
* Correspondence: bartashevichev@susu.ru;

Table S1. The energy characteristics of Hal⁻···CH_3–YR (Hal⁻ = Cl, Br) complexes taken from crystal structures with listed refcodes

Refcode	E_{com} [2]	E_{cat} [2]	E_{Hal} [2]	E_b [2]	ΔE_{BSSE} [3]	E_b* [4]
LONGEB (Y=N)	-1227.466350	-767.095777	-460.257420	-71.052830	-0.001526	-71.895402
TMHYZC (Y=N)	-690.470080	-230.081010	-460.257420	-82.668243	-0.001488	-83.217361
VAPREJ (Y=N)	-633.933164	-173.545474	-460.257420	-81.800417	-0.002269	-82.062672
ZENJAD (Y=O)	-993.217431	-532.876748	-460.257420	-52.282767	-0.001837	-53.577581
GETQIF (Y=N)	-635.155302	-174.768773	-460.257420	-81.072254	-0.001438	-81.495893
FADXIR (Y=N)	-3015.071263	-440.680183	-2574.261952	-81.086284	-0.000161	-81.598635
LILLOH (Y=N)	-2747.932725	-173.545490	-2574.261952	-78.670336	-0.000810	-78.901512
POSTUM02 (Y=N)	-2709.858138	-135.469081	-2574.261952	-79.815774	-0.000104	-80.207947
ZZZGVM01 (Y=N)	-2749.154832	-174.768716	-2574.261952	-77.967743	-0.000772	-78.343999
ZZZUQO03 (Y=N)	-2788.451625	-214.067645	-2574.261952	-76.626898	-0.000749	-77.006447

[1] R – residual fragments of cations in crystals with corresponding refcodes

[2] Notations are same as in Calculations section

[3] The value of BSSE correction $\Delta E_{BSSE} = E_b{}^*_{BSSE} - E_b{}^*$, where $E_b{}^*_{BSSE}$ – the binding energy between halide anion and cation with non-relaxed structures as in optimized complex with BSSE correction

[4] $E_b{}^*$ – the binding energy between halide anion and cation with non-relaxed structure as in optimized complexes

Table S2. Experimental and calculated tetrel and C–Y bond lengths D (Å), angles Hal⁻···C–Y and electron density (a.u.) at bond critical points for considered crystal and cation structures calculated in CRYSTAL code

Crystal	Bond	Crystal D_{exp}, Θ $(Hal^-\cdots C–N)_{exp}$	Crystal D_{calc}, Θ $(Hal^-\cdots C–N)_{calc}$	$\varrho(r_{bcp})$, crystal	Cation D_{calc}	$\varrho(r_{bcp})$, cation
GETQIF	Cl(3)⁻···C(2)	3.4584	3.4260	0.0056	–	–

		169.08	163.91			
	C(2)–N(1)	1.4815	1.4958	0.2441	1.505	0.2368
LONGEB	Cl(1)⁻···C(4)	3.4251 175.28	3.4087 166.64	0.0068	–	–
	C(4)–N(2)	1.4722	1.4740	0.2458	1.478	0.2450
VAPREJ	Cl(1)⁻···C(1)	3.417 164.88	3.4385 164.49	0.0064	–	–
	C(1)–N(1)	1.466	1.4747	0.2480	1.479	0.2442
TMHYZC	Cl(1)⁻···C(2)	3.4374 174.96	3.4280 176.34	0.0062	–	–
	C(2)–N(1)	1.4976	1.5080	0.2406	1.508	0.2413
ZENJAD	Cl(1)⁻···C(7)	3.5111 170.58	3.4644 171.72	0.0056	–	–
	C(7)–O(2)	1.4471	1.4468	0.2306	1.451	0.2270
JIBDED01	Br(1)⁻···C(1)	3.4915 173.25	3.4436 173.24	0.0070	–	–
	C(1)–N(1)	1.4926	1.5015	0.2490	1.519	0.2261
LILLOH	Br(1)⁻···C(2)	3.533 167.25	3.5664 166.86	0.0061	–	–
	C(2)–N(1)	1.474	1.4735	0.2490	1.479	0.2442
FADXIR	Br(1)⁻···C(6)	3.6014 170.87	3.5722 173.15	0.0058	–	–
	C(6)–N(1)	1.5025	1.5082	0.2371	1.506	0.2389
POSTUM02	Br(1)⁻···C(1)	3.7012 175.21	3.6667 174.15	0.0048	–	–
	C(1)–N(1)	1.4852	1.4928	0.2432	1.509	0.2304
ZZZGVM01	Br(1)⁻···C(2)	3.742 168.65	3.7283 169.04	0.0042	–	–
	C(2)–N(1)	1.474	1.4968	0.2437	1.505	0.2368
ZZZUQO03	Br(1)⁻···C(1)	3.685 171.12	3.6819 171.11	0.0049	–	–
	C(1)–N(1)	1.487	1.5039	0.2411	1.506	0.2399

Table S3. Bond lengths D(Å), the characteristics of electron density, potential and kinetic energy densities (a.u.), electrostatic potential (a.u.), potential acting on an electron in molecule PAEM at bcp (a.u.) for $Hal^{-}\cdots CH_3$ and Y–C bonds in complexes and cations calculated in GAMESS code

Refcode	Bond	D in complex	D in cations	$\varrho(r_{bcp})$ in complex	$\varrho(r_{bcp})$ in cation	$v(r_{bcp})$	$g(r_{bcp})$	$ESP(r_{bcp})$	$PAEM(r_{bcp})$
GETQIF	Cl⁻···C	2.8262		0.019		0.0161	-0.0131	0.0022	-0.4944
	N–C	1.5218	1.4947	0.214	0.235	0.1509	-0.3922	1.2734	
LONGEB	Cl⁻···C	2.8782		0.017		0.0147	-0.0116	-0.0246	-0.4569
	N–C	1.4930	1.4698	0.221	0.242	0.1801	-0.4520	1.3820	
TMHYZC	Cl⁻···C	2.8248		0.019		0.0164	-0.0133	0.0068	-0.5004
	N–C	1.5185	1.4975	0.220	0.239	0.1491	-0.3980	1.2583	
VAPREJ	Cl⁻···C	2.8226		0.019		0.0167	-0.0135	0.0076	-0.5006
	N–C	1.4859	1.4722	0.225	0.241	0.2033	-0.4935	1.4894	
ZENJAD	Cl⁻···C	2.9268		0.015		0.0125	-0.0098	-0.0771	-0.3956
	O–C	1.4844	1.4422	0.196	0.224	0.2124	-0.4483	1.4698	
FADXIR	Br⁻···C	2.9855		0.017		0.0134	-0.0110	0.0145	-0.4865

LILLOH	N–C	1.5220	1.4956	0.216	0.237	0.1459	-0.3859	1.2596	
	Br⁻···C	2.9896		0.016		0.0135	-0.0109	0.0126	-0.4808
POSTUM02	N–C	1.4835	1.4721	0.226	0.241	0.2029	-0.4963	1.4942	
	Br⁻···C	2.9802		0.017		0.0135	-0.0109	0.0139	-0.4841
ZZZGVM01	N–C	1.5259	1.4975	0.209	0.229	0.1531	-0.3874	1.3011	
	Br⁻···C	2.9949		0.0165		0.0129	-0.0105	0.0042	-0.4727
ZZZUQO03	N–C	1.5196	1.4949	0.2155	0.235	0.1505	-0.3941	1.2790	
	Br⁻···C	3.0015		0.0162		0.0129	-0.0104	0.0056	-0.4702
	N–C	1.4959	1.4959	0.2187	0.238	0.1443	-0.3881	1.2406	

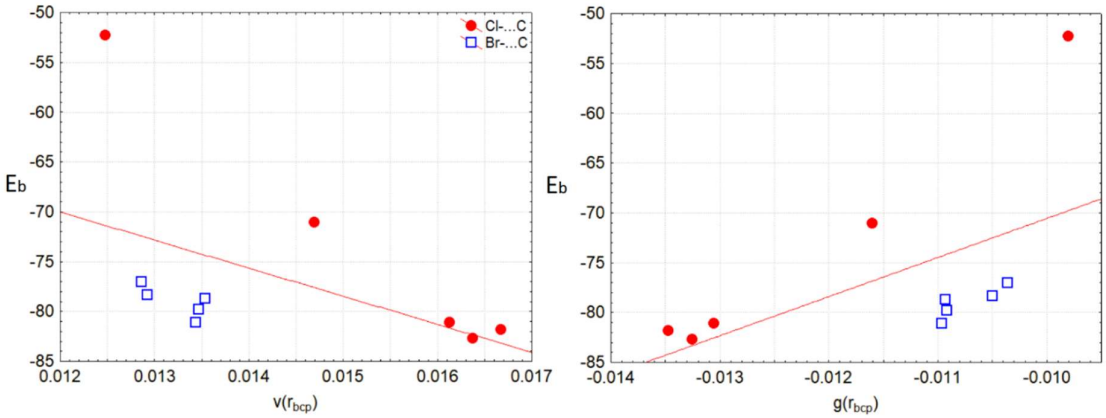

Figure S1. Binding energy (kcal/mol) in complexes vs the potential (a) and kinetic (b) energy density (a.u.) at the bond critical point of tetrel bonds

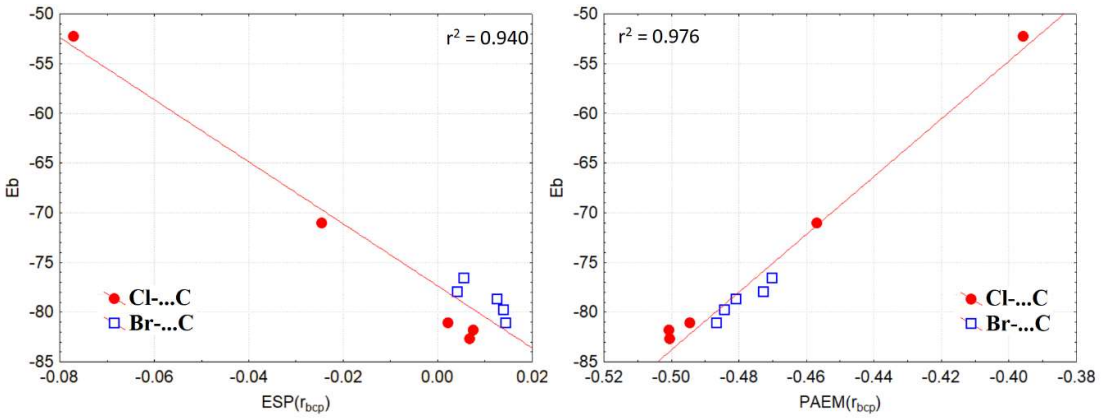

Figure S2. Binding energy (kcal/mol) in complexes vs the electrostatic potential (a.u.) (a) and (b), potential acting on an electron in molecule (a.u.) at the bond critical point of tetrel bon

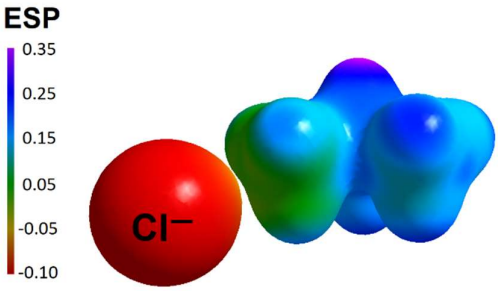

Figure S3. ESP in the trimethylammonium chloride on the isosurface of electron density of 0.02 a.u.