Supplementary Information

SMALL CARBIDES OF THIRD-ROW MAIN GROUP ELEMENTS: STRUCTURE AND BONDING IN C_3X COMPOUNDS (X=K-Br)

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Table S1. Summary of critical point data (in a.u.) for the linear isomers of C_3X species, using the QCISD/aug-cc-pVTZ electronic density.

Type		K ($^2\Pi$)	Ca($^3\Pi$)	Ga($^2\Pi$)	Ge($^3\Sigma^-$)	As($^2\Pi$)	Se($^1\Sigma^+$)	Br($^2A'$)
X-C_1 bond	$\rho(r)$	0.0305	0.0481	0.0910	0.1505	0.1879	0.2156	0.1962
	$\nabla^2\rho(r)$	0.1083	0.1644	0.2071	0.3656	0.3279	0.2614	-0.2216
	$-H(r)$	0.0270	0.0497	0.1233	0.0892	0.1362	0.4458	0.2546
C_1-C_2 bond	$\rho(r)$	0.3840	0.3894	0.3935	0.3778	0.3706	0.3661	0.3703
	$\nabla^2\rho(r)$	-1.4651	-1.4802	-1.4860	-1.4133	-1.3386	-1.0924	-1.4637
	$-H(r)$	0.7955	0.8227	0.8306	0.5431	0.5102	0.8816	0.7293
C_2-C_3 bond	$\rho(r)$	0.3656	0.3632	0.3607	0.3714	0.3906	0.3899	0.3785
	$\nabla^2\rho(r)$	-1.4115	-1.4089	-1.4026	-1.4580	-1.5403	-1.5685	-1.2904
	$-H(r)$	0.6950	0.6805	0.6680	0.5697	0.5751	0.8170	0.8332

Table S2. Summary of critical point data (in a.u.) for the fan isomers of C_3X species, using the QCISD/aug-cc-pVTZ electronic density.

Type		K ($^2B_2$)	Ca($^3B_1$)	Ga($^2B_2$)	Ge($^1A_1$)	As($^2B_1$)	Se($^1A_1$)	Br($^2B_2$)
X-C_1 bond	$\rho(r)$		0.0529					-
X-C_2	$\nabla^2\rho(r)$		0.2175					-
	$-H(r)$		0.0646					-
X-C_3 bond	$\rho(r)$	0.0210		0.0494	0.0970	0.0973	0.1041	-
	$\nabla^2\rho(r)$	0.0905		0.1301	0.2422	0.1400	0.0946	-
	$-H(r)$	0.0188		0.0562	0.0433	0.0419	0.1237	-
C_1-C_3 bond	$\rho(r)$	0.3701	0.3461	0.3654	0.3432	0.3486	0.3545	-
C_2-C_3	$\nabla^2\rho(r)$	-1.4094	-1.1548	-1.3804	-1.2158	-1.2677	-1.3265	-
	$-H(r)$	0.7320	0.7227	0.7037	0.4860	0.4923	0.6663	-

Table S3. Summary of critical point data (in a.u.) for the three-membered ring isomers of C_3X species, using the QCISD/aug-cc-pVTZ electronic density.

Type		K ($^2A_1$)	Ca($^3B_2$)	Ga($^2A_1$)	Ge($^1A_1$)	As^2($^2B_1$)	Se($^1A_1$)	Br($^2B_2$)
X-C_1 bond	$\rho(r)$	0.0287	0.0477	0.0897	0.1490	0.1698	0.2109	0.1916
	$\nabla^2\rho(r)$	0.0952	0.1489	0.1587	0.2536	0.1630	0.1943	-0.2208
	$-H(r)$	0.0246	0.0471	0.1138	0.0913	0.1171	0.4157	0.233
C_1-C_2 bond	$\rho(r)$	0.3247	0.2789	0.3217	0.2662	0.2652	0.25167	0.2993
C_1-C_3	$\nabla^2\rho(r)$	-0.9265	-0.4374	-0.9249	-0.3950	-0.2461	0.0553	-0.5775
	$-H(r)$	0.5885	0.4995	0.5758	0.2882	0.2571	0.4109	0.6091
C_2-C_3 bond	$\rho(r)$		0.3485		0.3281	0.3711	0.3967	0.3334
	$\nabla^2\rho(r)$		-1.0954		-0.9837	-1.2858	-1.1487	-0.9477
	$-H(r)$		0.6468		0.4058	0.4976	0.7888	0.6018

Table S4. Summary of critical point data (in a.u.) for the rhombic isomers of C_3X species, using the QCISD/aug-cc-pVTZ electronic density.

Type		K ($^2A_1$)	Ca($^3A_1$)	Ga($^2A_1$)	Ge($^1A_1$)	As($^2B_1$)	Se($^1A_1$)	Br($^2B_2$)
X-C_1 bond	$\rho(r)$	0.0248	0.0374	0.0676	0.1215	0.1396	0.1533	0.0841
X-C_2	$\nabla^2\rho(r)$	0.1048	0.1578	0.0799	0.2517	0.1530	0.0188	0.0789
	$-H(r)$	0.0231	0.0401	0.0581	0.0647	0.0889	0.2123	0.0723
C_1-C_2 bond	$\rho(r)$				0.2506	0.2499	0.2531	
	$\nabla^2\rho(r)$				-0.2913	-0.2568	-0.2365	
	$-H(r)$				0.2408	0.2353	0.4103	
C_1-C_3 bond	$\rho(r)$	0.3282	0.3301	0.2373	0.2794	0.2752	0.2726	0.3160
C_2-C_3	$\nabla^2\rho(r)$	-0.9307	-0.9348	–0.9671	-0.6343	-0.5893	-0.5341	-0.8922
	$-H(r)$	0.6091	0.6180	0.3836	0.3125	0.3142	0.5081	0.6139

Table S5. C_3X Energy Decomposition Analysis (kcal/mol) for the linear isomers.

	C_3K ($^2\Pi$)		C_3Ca ($^3\Pi$)		C_3Ga ($^2\Pi$)		C_3Ge ($^3\Sigma^-$)		C_3As ($^2\Pi$)		C_3Se ($^1\Sigma^+$)		C_3Br ($^2\Pi$)	
ΔE_{int}	-88.0		-98.0		-62.7		-90.6		-124.7		-150.3		-363.8	
ΔE_{pauli}	23.7		71.8		109.2		211.3		287.3		311.0		250.0	
ΔE_{elstat}	-17.9	(16.0%)[a]	-48.6	(28.6%)[a]	-64.8	(37.7%)[a]	-128.5	(42.6%)[a]	-168.9	(41.0%)[a]	-188.5	(40.9%)[a]	-159.6	(26.0%)[a]
ΔE_{orb}	-93.8	(84.0%)	-121.2	(71.4%)	-107.1	(62.3%)	-173.4	(57.4%)	-243.1	(59.0%)	-272.8	(59.1%)	-454.1	(74.0%)
$\Delta E(\sigma)$	-5.8	(6.1%)[b]	-17.7	(14.6%)[b]	-37.4	(34.9%)[b]	-76.5	(44.1%)[b]	-113.9	(46.9%)[b]	-152.8	(56.0%)[b]	-200.6	(44.2%)[b]
$\Delta E(\pi)$	-88.0	(93.9%)	-103.5	(85.4%)	-69.6	(65.0%)	-96.8	(55.8%)	-129.1	(53.1%)	-120.0	(44.0%)	-253.5	(55.8%)
$\Delta E(\delta)$	0.0	(0.0%)	0.0	(0.0%)	-0.1	(0.1%)	-0.1	(0.1%)	-0.1	(0.0%)	-0.1	(0.0%)	0.0	(0.0%)

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.
[b] Values in parentheses give the percentage contribution to the total orbital interactions.

Table S6. C_3X Energy Decomposition Analysis (kcal/mol) for the fan isomers.

	C_3K ($^2B_2$)		C_3Ca ($^3B_1$)		C_3Ga ($^2B_2$)		C_3Ge ($^1A_1$)		C_3As ($^2B_1$)		C_3Se ($^1A_1$)	
ΔE_{int}	-89.3		-169.7		-57.6		-107.1		-92.0		-79.5	
ΔE_{pauli}	36.7		126.9		108.8		268.1		242.6		197.7	
ΔE_{elstat}	-12.0	(9.6%)[a]	-49.3	(16.6%)[a]	-47.1	(28.3%)[a]	-125.9	(33.6%)[a]	-106.5	(31.8%)[a]	-81.6	(29.4%)[a]
ΔE_{orb}	-114.0	(90.4%)	-247.2	(83.4%)	-119.3	(71.7%)	-249.2	(66.4%)	-228.1	(68.2%)	-195.6	(70.6%)
$\Delta E(a_1)$	-4.4	(3.9%)[b]	-11.3	(4.6%)[b]	-20.9	(17.5%)[b]	-59.4	(23.8%)[b]	-74.7	(32.7%)[b]	-88.1	(45.0%)[b]
$\Delta E(a_2)$	0.0	(0.0%)	-94.3	(38.1%)	0.0	(0.0%)	-0.1	(0.0%)	0.0	(0.0%)	0.0	(0.0%)
$\Delta E(b_1)$	-0.9	(0.8%)	-4.2	(1.7%)	-3.6	(3.0%)	-15.1	(6.1%)	-13.0	(5.7%)	-8.1	(4.2%)
$\Delta E(b_2)$	-108.6	(95.3%)	-137.4	(55.6%)	-94.8	(79.5%)	-174.6	(70.1%)	-140.0	(61.6%)	-99.4	(50.8%)

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.
[b] Values in parentheses give the percentage contribution to the total orbital interactions.

Table S7. C_3X Energy Decomposition Analysis (kcal/mol) for the 3-ring isomers.

	C_3K ($^2A_1$)		C_3Ca ($^3B_2$)		C_3Ga ($^2A_1$)		C_3Ge ($^1A_1$)		C_3As ($^2B_1$)		C_3Se ($^1A_1$)		C_3Br ($^2B_2$)	
ΔE_{int}	-91.6		-60.5		-66.3		-82.1		-81.2		-109.9		-75.2	
ΔE_{pauli}	20.2		95.0		102.1		275.7		318.3		367.7		235.5	
ΔE_{elstat}	-12.1	(10.8%)[a]	-54.5	(35.1%)[a]	-56.6	(33.6%)[a]	-152.9	(42.7%)[a]	-171.9	(43.0%)[a]	-194.4	(40.7%)[a]	-129.8	(41.8%)[a]
ΔE_{orb}	-99.7	(89.2%)	-101.0	(64.9%)	-111.8	(66.4%)	-204.9	(57.3%)	-227.6	(57.0%)	-283.3	(59.3%)	-180.9	(58.2%)
$\Delta E(a_1)$	-5.6	(5.6%)[b]	-95.8	(94.8%)[b]	-44.2	(39.6%)[b]	-161.6	(78.9%)[b]	-172.5	(75.8%)[b]	-193.7	(68.4%)[b]	-151.1	(83.5%)[b]
$\Delta E(a_2)$	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)
$\Delta E(b_1)$	-0.8	(0.8%)	-2.2	(2.2%)	-3.1	(2.8%)	-10.0	(4.9%)	-22.8	(10.0%)	-41.8	(14.8%)	-17.5	(9.7%)
$\Delta E(b_2)$	-93.2	(93.5%)	-3.0	(3.0%)	-64.4	(57.6%)	-33.4	(16.3%)	-32.3	(14.2%)	-47.8	(16.9%)	-12.3	(6.8%)

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.
[b] Values in parentheses give the percentage contribution to the total orbital interactions.

Table S8. C_3X Energy Decomposition Analysis (kcal/mol) for the rhombic isomers.

	C_3K ($^2A_1$)		C_3Ca ($^3A_1$)		C_3Ga ($^2A_1$)		C_3Ge ($^1A_1$)		C_3As ($^2B_1$)		C_3Se ($^1A_1$)		C_3Br ($^2B_2$)	
ΔE_{int}	-109.9		-133.8		-87.6		-102.5		-84.4		-82.8		-61.0	
ΔE_{pauli}	25.1		93.7		110.9		410.3		423.63		393.5		134.9	
ΔE_{elstat}	-12.8	(9.5%)[a]	-54.1	(23.8%)[a]	-58.6	(29.5%)[a]	-201.9	(39.4%)[a]	-199.6	(39.3%)[a]	-179.8	(37.8%)[a]	-64.8	(33.1%)[a]
ΔE_{orb}	-122.1	(90.5%)	-173.4	(76.2%)	-139.9	(70.5%)	-311.0	(60.6%)	-308.5	(60.7%)	-296.5	(62.3%)	-131.1	(66.9%)
$\Delta E(a_1)$	-3.1	(2.6%)[b]	-27.61	(15.9%)[b]	-29.5	(21.1%)[b]	-194.5	(62.5%)[b]	-188.2	(61.0%)[b]	-173.9	(58.7%)[b]	-85.3	(65.1%)[b]
$\Delta E(a_2)$	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)	0.0	(0.0%)
$\Delta E(b_1)$	-0.5	(0.4%)	-2.25	(1.3%)	2.6	(1.8%)	-13.5	(4.3%)	-20.5	(6.6%)	-22.5	(7.6%)	-4.6	(3.5%)
$\Delta E(b_2)$	-118.6	(97.0%)	-143.5	(82.8%)	-107.8	(77.0%)	-103.0	(33.1%)	-99.7	(32.3%)	-100.0	(33.7%)	-41.2	(31.4%)

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.
[b] Values in parentheses give the percentage contribution to the total orbital interactions.