Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Symmetry breaking in the planar configurations of disilicontetrahalides. Pseudo Jahn-Teller effect parameters, hardness and electronegativity

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Table SI-1. LC-BLYP/Def2-TZVPP, LC-ωPBE/Def2-TZVPP and B3LYP/Def2-TZVPP calculated corrected electronic energies (E_o=E_{el}+*ZPE*) [zero point energies (*ZPE*) from B3LYP/Def2-TZVPP level] for the planar (D_{2h} symmetry) and bent (C_{2h} symmetry) geometries of compounds **1-4**.

Method	LC-BLYP/Def2-TZVPP			LC-ωPBE/Def2-TZVPP			B3LYP/Def2-TZVPP		
	ZPE	E_0	ΔE_0^a	*ZPE*	E_0	ΔE_0^a	*ZPE*	E_0	ΔE_0^a
compound									
1, C_{2h}	0.010945	-977.720106	0.00	0.011243	-978.325617	0.00	0.011062	-978.789737	0.00
1, D_{2h}	0.013279	-977.672125	30.11	0.012978	-978.282672	26.95	0.012652	-978.731386	36.62
2, C_{2h}	0.007894	-2418.519307	0.00	0.007967	-2419.291896	0.00	0.007288	-2420.099696	0.00
2, D_{2h}	0.008782	-2418.503821	9.72	0.008707	-2419.278261	8.56	0.008152	-2420.069176	19.15
3, C_{2h}	0.006303	-10873.755558	0.00	0.006360	-10874.132689	0.00	0.005644	-10875.913622	0.00
3, D_{2h}	0.006971	-10873.743436	7.61	0.006902	-10874.122226	6.56	0.006350	-10875.885970	17.35
4, C_{2h}	0.005534	-1768.549434	0.00	0.005588	-1769.887986	0.00	0.004864	-1770.373083	0.00
4, D_{2h}	0.005878	-1768.542280	4.49	0.005848	-1769.881968	3.78	0.005336	-1770.351212	13.72

Table SI-2. Calculated structural parameters of the planar (D_{2h}) and *trans*-bent (C_{2h}) geometries of compounds **1-4**.

Compound	**1**		**2**		**3**		**4**	
Geometry	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}
Bond lengths (Å)								
$r_{si\text{-}si}$	(2.049)[a]	(2.844)[a]	(2.069)[a]	(2.329)[a]	(2.076))[a]	(2.290)[a]	(2.088)[a]	(2.227)[a]
	(2.064)[b]	(2.641)[b]	(2.083)[b]	(2.311)[b]	(2.090)[b]	(2.273)[b]	(2.101)[b]	(2.220)[b]
	(2.084)[c]	(2.638)[c]	(2.113)[c]	(2.426)[c]	(2.123)[c]	(2.404)[c]	(2.140)[c]	(2.365)[c]
	(2.048)[d]			(2.343)[e]				
$r_{si\text{-}x}$	(1.570)[a]	(1.588)[a]	(2.006)[a]	(2.035)[a]	(2.164)[a]	(2.194)[a]	(2.381)[a]	(2.409)[a]
	(1.581)[b]	(1.598)[b]	(2.012)[b]	(2.038)[b]	(2.170)[b]	(2.197)[b]	(2.385)[b]	(2.409)[b]
	(1.584)[c]	(1.604)[c]	(2.036)[c]	(2.076)[c]	(2.204)[c]	(2.249)[c]	(2.429)[c]	(2.477)[c]
	(1.591)[d]			(2.056)[e]				
$\Delta[r_{si\text{-}si}(C_{2h}) - r_{si\text{-}si}(D_{2h})]$[a]	0.795		0.260		0.214		0.139	
$\Delta[r_{si\text{-}si}(C_{2h}) - r_{si\text{-}si}(D_{2h})]$[b]	0.577		0.228		0.183		0.119	
$\Delta[r_{si\text{-}si}(C_{2h}) - r_{si\text{-}si}(D_{2h})]$[c]	0.554		0.313		0.281		0.225	
Bond angles (°)								
$\theta_{x\text{-}si\text{-}si}$	(125.5)[a]	(105.5)[a]	(123.6)[a]	(111.6)[a]	(122.8)[a]	(112.3)[a]	(121.8)[a]	(113.9)[a]
	(125.3)[b]	(106.6)[b]	(123.2)[b]	(112.1)[b]	(122.7)[b]	(112.8)[b]	(121.7)[b]	(114.2)[b]
	(125.1)[c]	(106.7)[c]	(123.0)[c]	(110.2)[c]	(122.5)[c]	(110.4)[c]	(121.7)[c]	(111.1)[c]
$\theta_{x\text{-}si\text{-}x}$	(109.1)[a]	(101.3)[a]	(113.3)[a]	(106.1)[a]	(114.4)[a]	(107.6)[a]	(116.3)[a]	(110.4)[a]
	(109.5)[b]	(102.3)[b]	(113.5)[b]	(106.8)[b]	(114.6)[b]	(108.2)[b]	(116.6)[b]	(110.9)[b]
	(109.8)[c]	(102.8)[c]	(114.0)[c]	(106.1)[c]	(115.1)[c]	(107.3)[c]	(116.7)[c]	(109.0)[c]
	(109.7)[d]							
Torsion angles (°)								
$\theta_{x\text{-}si\text{-}si\text{-}x}$	(0.0)[a]	(73.3)[a]	(0.0)[a]	(61.5)[a]	(0.0)[a]	(58.6)[a]	(0.0)[a]	(52.2)[a]
	(0.0)[b]	(71.3)[b]	(0.0)[b]	(60.0)[b]	(0.0)[b]	(57.0)[b]	(0.0)[b]	(50.8)[b]
	(0.0)[c]	(70.5)[c]	(0.0)[c]	(63.3)[c]	(0.0)[c]	(61.5)[c]	(0.0)[c]	(58.4)[c]
Flap Angles (°)								
	(0.0)[a]	(65.1)[a]	(0.0)[a]	(52.3)[a]	(0.0)[a]	(50.0)[a]	(0.0)[a]	(44.8)[a]
	(0.0)[b]	(62.9)[b]	(0.0)[b]	(51.0)[b]	(0.0)[b]	(48.6)[b]	(0.0)[b]	(43.7)[b]
	(0.0)[c]	(62.4)[c]	(0.0)[c]	(55.1)[c]	(0.0)[c]	(53.9)[c]	(0.0)[c]	(51.6)[c]

[a] From LC-BLYP/Def2-TZVPP [this work]. [b] From LC-wPBE/Def2-TZVPP [this work]. [c] From B3LYP/Def2-TZVPP [this work]. [d] From HF/DZd, see Ref. 15**.** [e]From MP2/6-31G(d,p), see Ref. 18.

Table SI-3. LC-ωPBE/Def2-TZVPP calculated energies (in hartree) of HOMO (ε_{HOMO}), LUMO (ε_{LUMO}), ε_{LUMO}-ε_{HOMO}, global hardness (η), global electronegativity (χ), $\Delta[\eta(C_{2h})\text{-}\eta(D_{2h})]$ and $\Delta[\chi(C_{2h})\text{-}\chi(D_{2h})]$ parameters for the *trans*-bent (C_{2h}) and planar (D_{2h}) configurations of compounds **1-4**.

compound	ε_{HOMO}	ε_{LUMO}	ε_{LUMO} - ε_{HOMO}	I	A	η	χ	$\Delta[\eta(C_{2h})\text{-}\eta(D_{2h})]$	$\Delta[\chi(C_{2h})\text{-}\chi(D_{2h})]$
1, C_{2h}	-0.35420	-0.05145	0.30275	0.35420	0.05145	0.15137	0.20282	-0.01082(-6.79)[a]	0.05645 (35.4)[a]
1, D_{2h}	-0.30856	0.01582	0.32438	0.30856	-0.01582	0.16219	0.14637	0.00000	0.00000
2, C_{2h}	-0.32112	-0.05677	0.26435	0.32112	0.05677	0.13217	0.18894	-0.02697(-16.92)[a]	0.04916 (30.8)[a]
2, D_{2h}	-0.29892	0.01936	0.31828	0.29892	-0.01936	0.15914	0.13978	0.00000	0.00000
3, C_{2h}	-0.31539	-0.06006	0.25533	0.31539	0.06006	0.12766	0.18772	-0.02132 (-13.38)[a]	0.03994 (25.1)[a]
3, D_{2h}	-0.29676	0.00120	0.29796	0.29676	-0.00120	0.14898	0.14778	0.00000	0.00000
4, C_{2h}	-0.30234	-0.05751	0.24483	0.30234	0.05751	0.12241	0.12241	-0.01364(-8.56)[a]	0.03093(19.4)[a]
4, D_{2h}	-0.28939	-0.01729	0.27210	0.28939	0.01729	0.13605	0.15334	0.00000	0.00000

Table SI-4. LC-BLYP/Def2-TZVPP calculated energies (in hartree) of HOMO (ε_{HOMO}), LUMO (ε_{LUMO}), ε_{LUMO}-ε_{HOMO}, global hardness (η), global electronegativity (χ), $\Delta[\eta(C_{2h})$-$\eta(D_{2h})]$ and $\Delta[\chi(C_{2h})$-$\chi(D_{2h})]$ parameters for the *trans*-bent (C_{2h}) and planar (D_{2h}) configurations of compounds **1-4**.

compound	ε_{HOMO}	ε_{LUMO}	ε_{LUMO} - ε_{HOMO}	I	A	η	χ	$\Delta[\eta(C2h)$-$\eta(D2h)]$	$\Delta[\chi(C_{2h})$-$\chi(D_{2h})]$
1, C_{2h}	-0.36963	-0.04456	0.32507	0.36963	0.04456	0.16254	0.20709	-0.00259(-1.63)[a]	0.06065 (38.1)[a]
1, D_{2h}	-0.31156	0.01869	0.33025	0.31156	-0.01869	0.16513	0.14644	0.00000	0.00000
2, C_{2h}	-0.32517	-0.05638	0.26879	0.32517	0.05638	0.13439	0.19077	-0.02867(-17.99)[a]	0.0532 (33.4)[a]
2, D_{2h}	-0.30062	0.02549	0.32611	0.30062	-0.02549	0.16306	0.13757	0.00000	0.00000
3, C_{2h}	-0.31961	-0.06074	0.25887	0.31961	0.06074	0.12943	0.19017	-0.02258 (-14.17)[a]	0.04319 (27.1)[a]
3, D_{2h}	-0.29899	0.00503	0.30402	0.29899	-0.00503	0.15201	0.14698	0.00000	0.00000
4, C_{2h}	-0.30536	-0.05736	0.24800	0.30536	0.05736	0.12400	0.18136	-0.01372 (-8.61)[a]	0.0278(17.4)[a]
4, D_{2h}	-0.29128	-0.01585	0.27543	0.29128	0.01585	0.13772	0.15357	0.00000	0.00000