Electronic Supplementary Material (ESI) for CrystEngComm.

Alkyl Groups as Electron Density Donors in π-hole Bonding

Jorge Echeverría

Departament de Química Inorgànica i Orgànica and Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona (Spain).

e-mail: jorge.echeverria@qi.ub.es

SUPPORTING INFORMATION

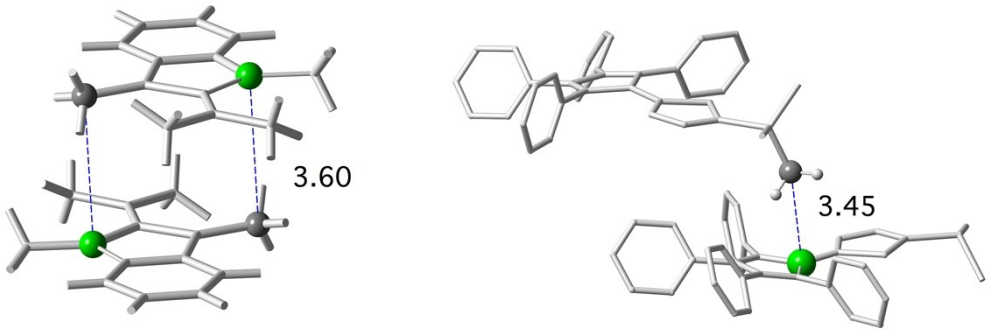

Figure S1. Short B···C(sp^3) contacts (Å) in the crystal structure of of 2,3-Benzo-1,4-dihydro-1,4,6,6-tetramethyl-1,4-diborafulvene (left, CSD refcode SINCOH) and of 1-(5-(trimethylsilyl)-2-thienyl)-2,3,4,5-tetraphenylborole (right, CSD refcode KEQGAQ).

Table S1. Calculated binding energies and intermolecular distances for the dimers of EH_3···CH_4 (E = B, Al, Ga). At the CCSD(T) level, all variables were kept frozen (at the fully optimized monomers) except the E···C distance, which was optimized. The aug-cc-pVTZ basis set was used for all atoms.

E	Method	E···C (Å)	E···H (Å)	H···H (Å)	ΔE_{BSSE} (kcal/mol)
B	CCSD(T)	3.018	2.854	2.895	-1.30
	MP2	3.014	2.850	2.893	-1.25
	B3LYP-D3	3.090	2.921	2.961	-1.45
	ωB97xD	3.015	2.851	2.895	-1.70
	M06-2X-D3	2.827	2.656	2.712	-2.28
	LC-ωPBE-D3BJ	3.016	2.852	2.897	-1.29
Al	CCSD(T)	2.962	2.794	2.960	-2.62
	MP2	2.910	2.771	2.945	-2.57
	B3LYP-D3	3.236	3.050	3.206	-1.99
	ωB97xD	2.968	2.806	2.985	-3.21
	M06-2X-D3	2.842	2.694	2.910	-4.20
	LC-ωPBE-D3BJ	2.761	2.620	2.837	-3.97
Ga	CCSD(T)	2.887	2.733	2.897	-1.76
	MP2	2.858	2.720	2.853	-1.59
	B3LYP-D3	3.338	3.154	3.284	-1.96
	ωB97xD	3.122	2.950	3.088	-2.60
	M06-2X-D3	2.920	2.761	2.939	-3.70
	LC-ωPBE-D3BJ	2.982	2.804	2.991	-2.48

Table S2. Cartesian coordinates of the optimized dimers characterized as true minima by frequencies analysis.

Dimer 1

B

c	-0.042499	-3.496890	-0.027963
b	0.043613	-0.515255	0.131541
h	-0.175682	-0.619030	1.294006
h	1.163540	-0.424234	-0.254544
h	-0.855906	-0.453107	-0.641259
h	0.272078	-4.085871	0.828434
h	-0.229026	-4.148114	-0.876967
h	-0.955665	-2.962031	0.219414
h	0.753797	-2.801688	-0.289931

Al

c	-0.031114	-3.465863	-0.040644
al	0.031711	-0.582215	0.148516
h	0.046447	-0.757822	1.719386
h	1.393776	-0.430450	-0.641390
h	-1.341083	-0.373134	-0.609263
h	-0.027282	-3.876824	0.963183
h	-0.056806	-4.261705	-0.779222
h	-0.928224	-2.860172	-0.177668
h	0.886826	-2.898035	-0.200167

Ga

ga	0.097817	-0.641187	0.133944
h	-0.120628	-0.713216	1.665436
h	1.535240	-0.483024	-0.426515
h	-1.115174	-0.535601	-0.822491
h	0.355102	-4.283152	0.398724
c	-0.088995	-3.432115	-0.108845
h	-0.504907	-3.731507	-1.064847
h	-0.875594	-3.019468	0.517254
h	0.717139	-2.716982	-0.292658

Dimer 2

B

c	-0.178919	-0.302229	0.052199
b	0.116446	0.204274	2.903765
h	1.304588	0.200542	2.891070
h	-0.472745	1.236163	2.896630
h	-0.479884	-0.819023	2.986713
c	0.058416	0.090511	-1.401927
h	-1.241280	-0.387659	0.273183
h	0.293034	-1.253988	0.289223

h	0.244843	0.462002	0.711326
h	-0.355698	-0.656582	-2.077517
h	-0.410949	1.045450	-1.632858
h	1.122148	0.180539	-1.616194

Al

c	1.001955	0.679826	0.010988
al	-1.695891	-0.133731	-0.006415
h	-1.197838	-1.473690	-0.685357
h	-1.932211	-0.093661	1.558707
h	-2.174527	1.078583	-0.902660
c	2.035889	-0.438042	-0.000977
h	1.453507	1.664323	0.124214
h	0.441842	0.706590	-0.926888
h	0.329621	0.570552	0.872026
h	2.737614	-0.303608	-0.822100
h	2.603420	-0.452844	0.927630
h	1.558088	-1.408446	-0.122247

Ga

c	-0.639491	-0.386328	0.013293
ga	0.396960	0.220048	2.477786
h	1.781636	-0.085216	1.852807
h	-0.078825	1.692838	2.588346
h	-0.403237	-0.899285	3.189738
c	0.245771	0.146348	-1.103070
h	-1.632723	-0.660570	-0.339540
h	-0.208546	-1.271671	0.478959
h	-0.822039	0.397021	0.761519
h	0.377372	-0.605303	-1.879391
h	-0.193139	1.030137	-1.562414
h	1.230031	0.414413	-0.723613