

Supplementary Information

Bifurcated triel bonds - hydrides and halides of 1,2-bis(dichloroboryl)benzene and 1,8-bis(dichloroboryl) naphthalene

by

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Table S1 Geometrical (Å and degrees) parameters corresponding to MP2/aug-cc-pVTZ and DFT-ADF optimizations (the latter ones in parentheses); in the case both B...H/X lengths are equal the one value is presented (and the corresponding ADF value in parentheses).

System	B...H/X bond length	B-(H/X)-B angle
Naphthalene skeleton		
BCIB	1.968(2.001)	102.2(102.3)
	1.952(1.986)	
BFB	1.540(1.570)	126.2(125.3)
	1.545(1.571)	
BHB	1.315(1.343)	140.6(139.1)
Benzene skeleton		
BCIB	1.991(2.044)	95.2(96.5)
BFB	1,569(1.601)	112.5(113.3)
BHB	1.360(1.387)	122.0(121.3)

Table S2 The T(H/X)T⁻ systems of the halide and hydride sponges taken from the Cambridge Structural Database, geometrical parameters of systems analysed are presented: the T...H/X distances, (subscripts, 1 and 2, correspond to two distances within one system considered) and the T-(H/X)-T angle; the refcodes of crystal structures as well as corresponding references are included.

Refcode	System	T...H/X ₁	T...H/X ₂	T-(H/X)-T	Ref.
The naphthalene skeleton					
AGIPAI	BFB	1.599	1.606	125.7	1
CUTFUS	BHB	1.487	1.201	142	2
CUTFUS10	BHB	1.487	1.201	142	3
EZAZOU	BFB	1.632	1.586	126	4
FIGRAO *	BClB	1.920	2.012	102	5
LUFCEV **	BHB	1.309	1.370	142.4	6
LUFCEV **	BHB	1.443	1.415	121.3	6
PERZES **	BFB	1.635	1.636	126.6	7
YIRHIQ	GaClGa	2.370	2.366	77.3	8
YIRHIQ	GaClGa	2.396	2.379	76.5	8
The benzene ring skeleton					
ECUGUF **	BFB	1.487	1.487	113.2	9
ETIMAX	BFB	1.596	1.62	111.2	10
	BFB	1.611	1.617	111.3	10
	BFB	1.589	1.624	111.9	10
GAYRUV	BClB	1.999	2.039	94.1	11
GOTNEI	AlClAl	2.281	2.278	98.3	12
	AlClAl	2.289	2.272	99.1	12
IQAJOZ	BClB	2.040	2.033	94.3	13
IQAJOZ01	BClB	2.036	2.041	94.3	10

* disorder concerns chlorine atoms

** disorder neither concerns triel atoms not their neighbours

Table S3 The T(H/X)T⁻ systems of the halide and hydride sponges taken from Cambridge Structural Database and considered in this study; the refcodes of crystal structures are included as well as the temperature of measurement (Temp), R-factors (residual indices) are presented and estimated standard deviations (e.s.d's) for CC bonds of the structure considered.

Refcode	R(%)	Temp	e.s.d
The naphthalene skeleton			
AGIPAI	9.53	110	0.006-0.010
CUTFUS	5.2	295	not recorded
CUTFUS10	5.2	295	0.011-0.030
EZAZOU	5.32	110	0.001-0.005
FIGRAO*	4.6	295	0.011-0.030
LUFCEV **	6.79	183	0.006-0.010
LUFCEV **	6.79	183	0.006-0.010
PERZES **	7.53	110	0.006-0.010
YIRHIQ	2.88	110	0.011-0.030
YIRHIQ	2.88	110	0.011-0.030
The benzene skeleton			
ECUFUF **	5.08	173	0.011-0.030
ETIMAX	4.31	160	0.001-0.005
GAYRUV	5.57	150	0.006-0.010
GOTNEI	3.59	173	0.006-0.010
IQAJOZ	4.68	150	0.001-0.005
IQAJOZ01	3.8	160	0.001-0.005

* disorder concerns chlorine atoms

** disorder neither concerns triel atoms not their neighbours

Fig. S1 The linear relationship between MP2 and DFT(ADF) results concerning B...H/X distances (in Å, designated in figure as bond lengths).

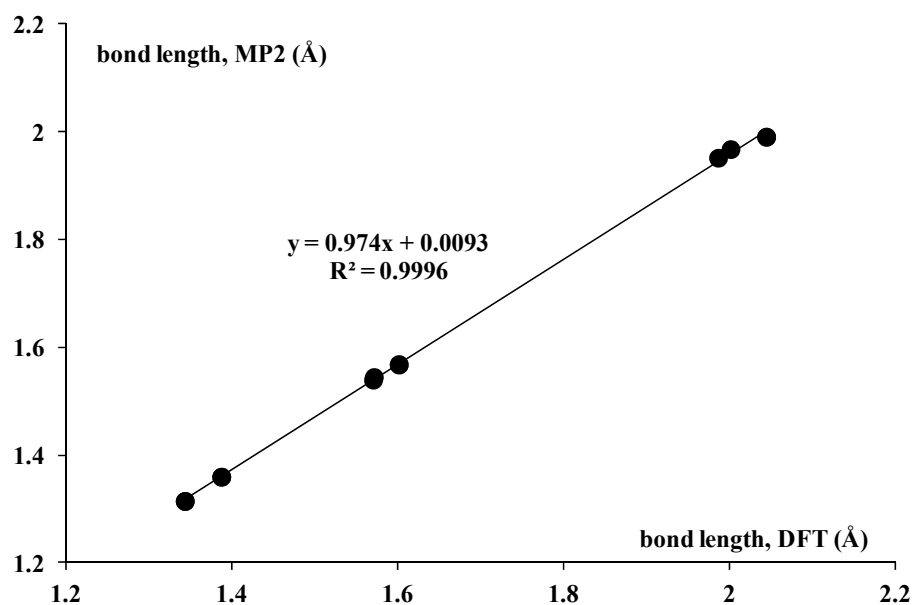


Fig. S2 The linear relationship between MP2 and DFT(ADF) results concerning B-(H/X)-B angles (in degrees).

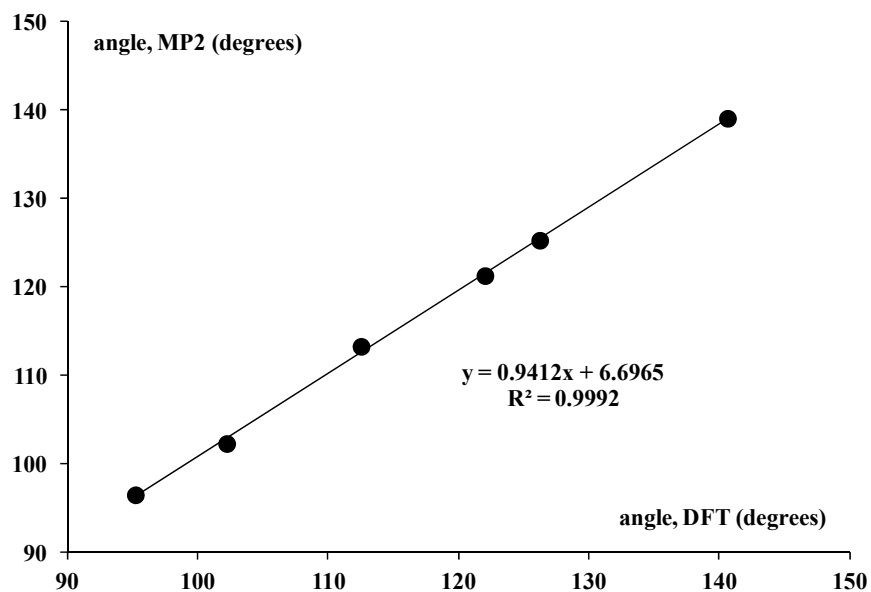


Fig. S3 The fragment of the crystal structure of tris(dimethylamino) sulfonium spiro (1,1-dimesityl-naphtho(1,8-cd)(1,2,6) fluoradiborinin-3,10'-phenoxaborine), PERZES refcode.

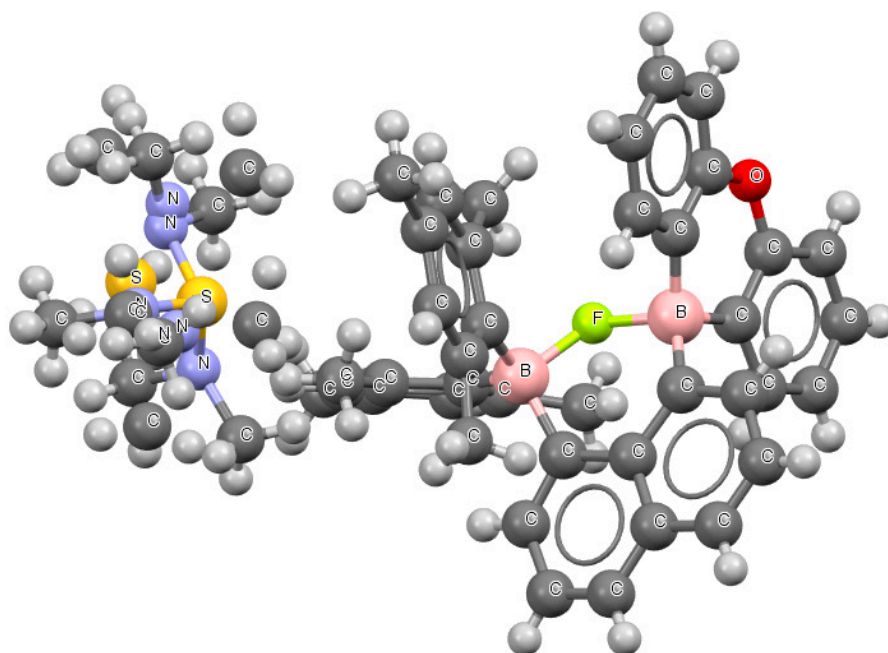


Fig. S4 The fragment of the crystal structure of bis(triphenylphosphine)-iminium 1,8-naphthalenediyl-bis(dichloroborane) chloride, FIGRAO refcode.

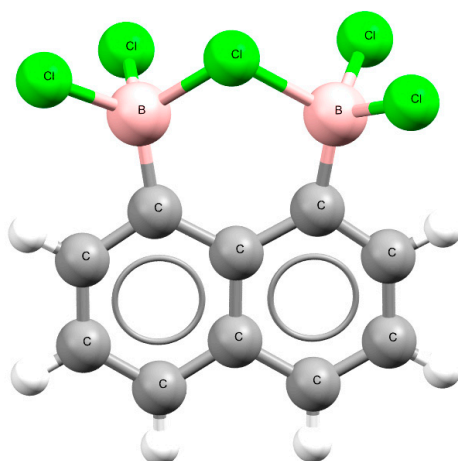


Fig. S5 The fragment of the crystal structure of potassium μ F-1,2-bis(difluoroboryl)tetrafluorobenzene acetonitrile solvate monohydrate, ECUGUF refcode.

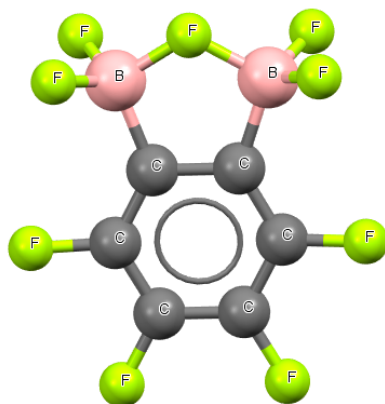
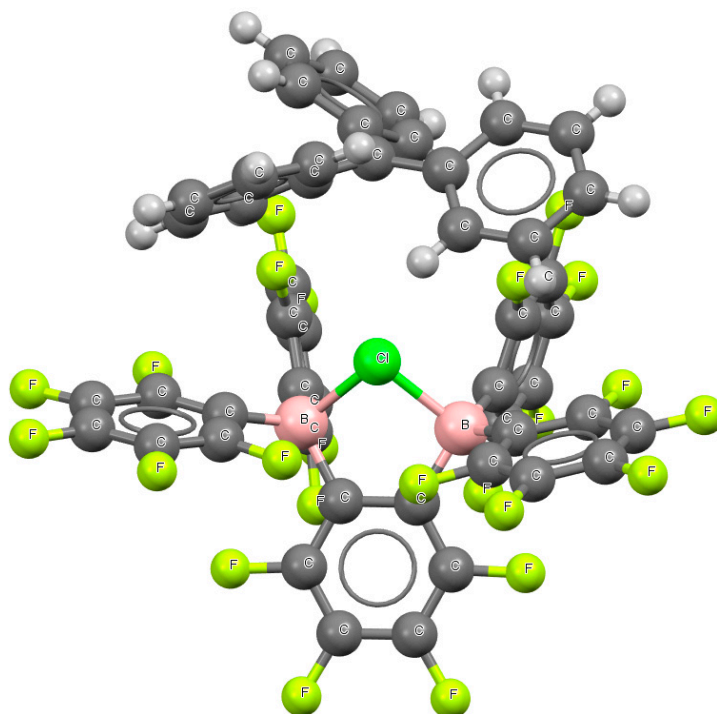


Fig. S6 The fragment of the crystal structure of triphenylcarbenium B,B'-(chloro)-3,4,5,6-tetrafluoro-1,2-bis(bis(pentafluorophenyl)boryl)benzene, IQAJ0Z01 refcode.



References related to Table S2

- 1 C.L. Dorsey, P. Jewula, T.W. Hudnall, J.D. Hoefelmeyer, T.J. Taylor, N.R. Honesty, C-W. Chiu, M. Schulte and F. Gabbai, *Dalton Trans.* 2008, 4442.
- 2 H.E. Katz, *J. Am. Chem. Soc.* 1985, **107**, 1420.
- 3 H.E. Katz, *J. Org. Chem.* 1985, **50**, 5027.
- 4 S. Sole and F.P. Gabbai, *Chem. Comm.* 2004, 1284.
- 5 H.E. Katz, *Organometallics* 1987, **6**, 1134.
- 6 C. Jiang, O. Blacque and H. Berke, *Chem. Comm.* 2009, 5518.
- 7 M. Melaimi, S. Solé, C-W. Chiu, H. Wang and F.P. Gabbai, *Inorg. Chem.* 2006, **45**, 8136.
- 8 J.D. Hoefelmeyer, D.L. Brode and F.P. Gabbai, *Organometallics* 2001, **20**, 5653.
- 9 P.A. Chase, L.D. Henderson, W.E. Piers, M. Parvez, W. Clegg and M.R.J. Elsegood, *Organometallics* 2006, **25**, 349.
- 10 W. Clegg, 2016, *CSD Communication*, private communication.
- 11 M.J. Sgro, J. Domer and D.W. Stephan, *Chem. Comm.* 2012, **48**, 7253.
- 12 M. Tschinkl, R.E. Bachman and F.P. Gabbai, *Chem. Comm.* 1999, 1367.
- 13 S.P. Lewis, N.J. Taylor, W.E. Piers and S. Collins, *J. Am. Chem. Soc.* 2003, **125**, 14686.