Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information for:

Exploring secondary bonding in p-block chemistry – an experimental study of [GeX_2{*o*-$C_6H_4(PMe_2)_2$}] using variable pressure single crystal X-ray diffraction

David R. Allan,[a] Simon J. Coles,[b] Kathryn George,[b] Marek Jura,[c] William Levason,[b] Gillian Reid,[b] Claire Wilson[a] and Wenjian Zhang[b]

Table S1: Unit Cell parameter details for [GeX_2{*o*-$C_6H_4(PMe_2)_2$}] X= Cl, Br, I

1 [$GeCl_2${*o*-$C_6H_4(PMe_2)_2$}]:

Pressure (kbar)	a (Å)	b (Å)	c (Å)	β (°)	Vol (Å^3)
1	27.82(8)	7.38(2)	13.96(4)	109.73(16)	2698(13)
14	27.691(16)	7.225(3)	13.704(4)	110.00(3)	2576(2)
30	27.380(8)	7.0724(14)	13.445(2)	110.187(15)	2443.6(9)
11	27.99(4)	7.325(10)	13.88(2)	110.29(8)	2669(7)
38	26.91(4)	6.962(8)	13.249(18)	110.30(7)	2328(5)
48	26.73(4)	6.863(8)	13.068(18)	110.22(7)	2250(5)

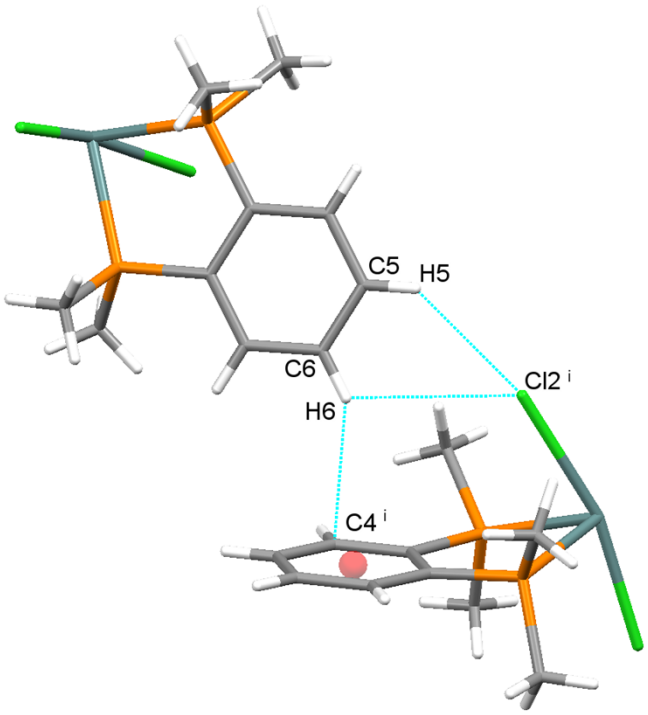
2 [$GeBr_2${*o*-$C_6H_4(PMe_2)_2$}]:

Pressure (kbar)	a (Å)	b (Å)	c (Å)	β (°)	Vol (Å^3)
0.001	29.46(4)	7.628(9)	14.510(17)	111.334(18)	3037(7)
2	29.22(4)	7.578(8)	14.434(18)	111.13(2)	2981(7)
11.1	28.41(3)	7.339(5)	14.008(13)	111.53(2)	2717(4)
27.3	27.88(3)	7.166(6)	13.692(13)	111.678(15)	2542(4)
41.5	25.79(10)	7.17(3)	14.06(5)	92.24(8)	2598(17)
53.7	24.773(10)	6.98(3)	13.67(5)	92.25(11)	2362(13)
63	24.73(6)	6.956(13)	13.63(3)	92.59(6)	2342(8)
80.1	24.56(16)	6.89(4)	13.52(8)	92.65(18)	2286(24)
93.6	24.30(13)	6.83(3)	13.37(7)	92.3(3)	2217(19)

3 [GeI_2{*o*-$C_6H_4(PMe_2)_2$}]:

Pressure (kbar)	a (Å)	b (Å)	c (Å)	β (°)	Vol (Å^3)
2	14.70(3)	7.589(11)	15.05(3)	117.45(3)	1490(4)
8	14.46(5)	7.41(2)	14.82(6)	117.18(6)	1412(8)
21	14.39(7)	7.34(3)	14.69(9)	117.26(11)	1379(11)
31	14.11(6)	7.20(3)	14.40(7)	117.27(11)	1300(10)
44	13.87(4)	7.08(2)	14.23(4)	117.13(6)	1244(6)
54	13.70(7)	7.01(3)	14.19(8)	117.11(12)	1213(10)
65	13.50(4)	6.92(2)	13.90(4)	116.92(6)	1157(5)
76	13.38(11)	6.85(4)	13.92(12)	116.9(2)	1137(14)
85	13.28(20)	6.81(8)	13.66(20)	117.2(3)	1099(3)

Table S2 Geometric details at the aromatic···aromatic interface



View illustrating aromatic···aromatic interface and atom labelling. Symmetry operation i = 3/2-x, 1/2+y, 3/2-z.

1:

Pressure		H6···C3-C8	
(kbar)	<C3_C8 planes (°)	centroid separation (Å)	<C6-H6···centroid (°)
1	80.82	2.941	154.8
14	77.13	2.781	148.42
30	76.02	2.715	146.03
11	78.37	2.869	150.18
38	74.6	2.648	144.67
48	73.16	2.585	143.33

2:

Pressure (kbar)	<C3_C8 planes (°)	H6···C3-C8 centroid separation (Å)	<C6-H6··· Centroid (°)	centroid-centroid separation (Å)	⊥ centroid-plane (Å)
0.001	75.71	3.065	158.3		
2	73.58	3.05	157.92		
11	74.84	2.836	151.36		
27	74.24	2.766	151.3		
41	0			3.911	2.773
54	0			3.885	2.763
63	0			3.919	2.809
80	0			3.884	2.686
94				3.822	2.45

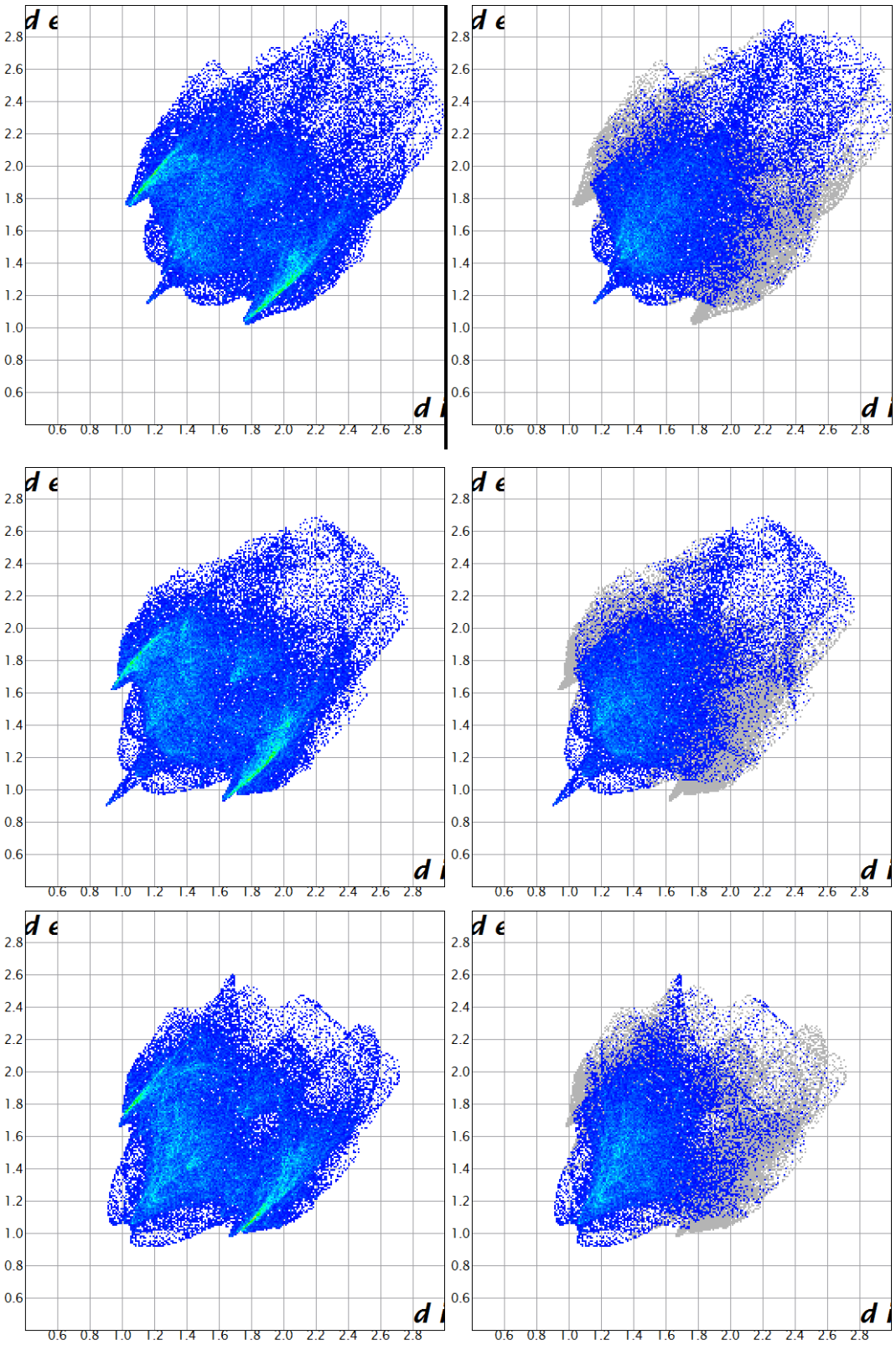


Figure S1: Fingerprint plots for **2** (d_{norm} surfaces) at ambient pressure (top), below (middle) and above the phase transition (bottom). Right hand side plots shows H···H contacts in blue.

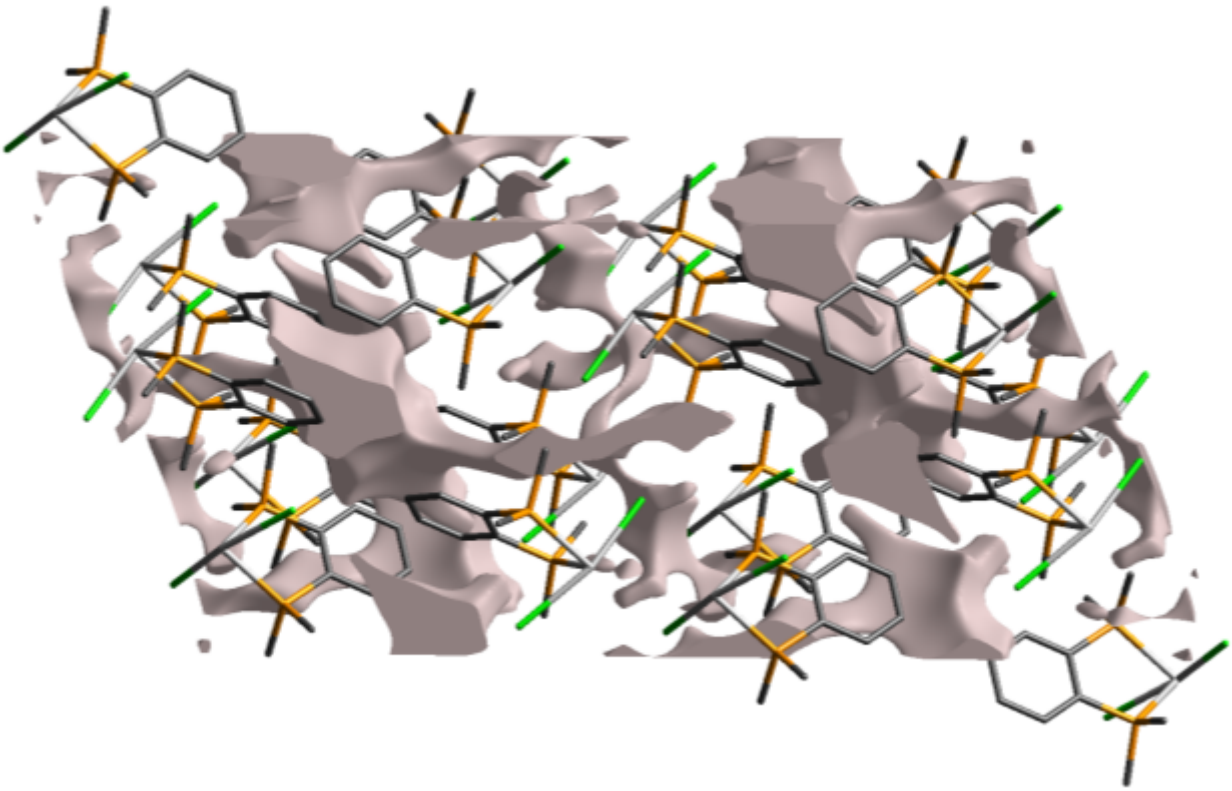


Figure S2: Void space in the structure of **1** at ambient pressure. The figure is oriented so that the two different interfaces, aromatic···aromatic and GeX_2···X_2Ge,are approximately vertical to illustrate that the void space is mostly in the aromatic···aromatic interface region.

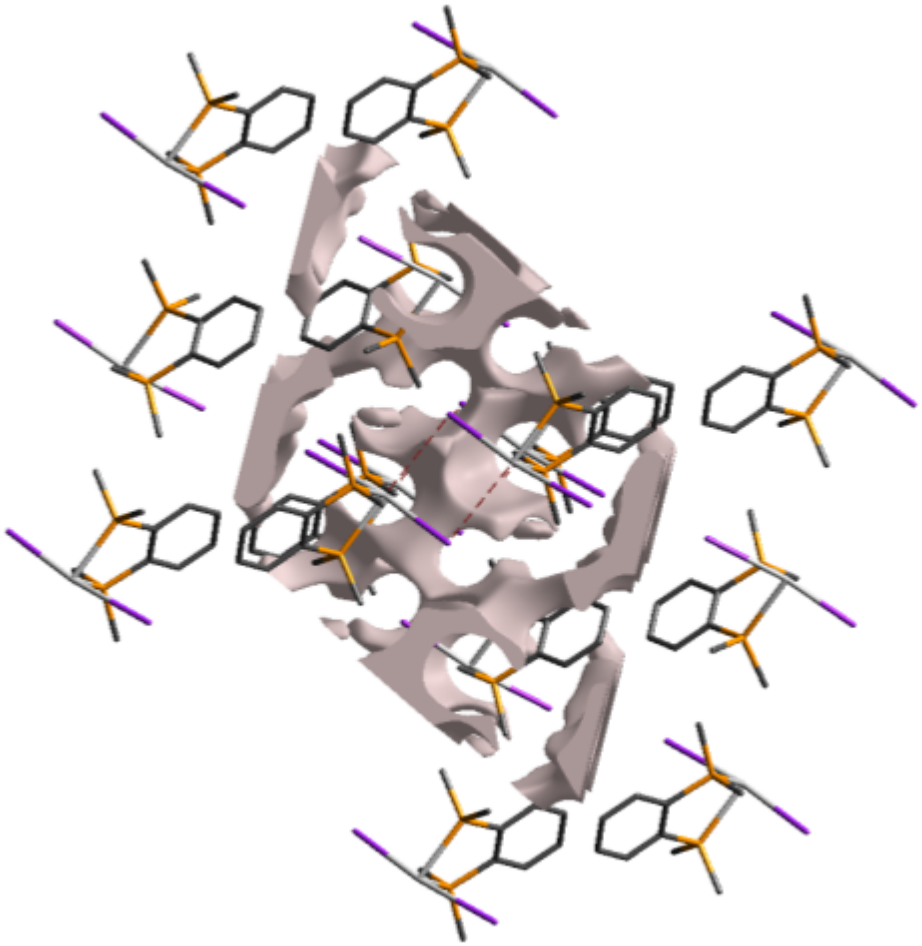


Figure S3: Void space in the structure of **3** at ambient pressure. The figure is oriented so that the two different interfaces, aromatic···aromatic and GeX_2···X_2Ge, are approximately vertical, illustrating that there is very little void space in either of these, but rather voids are located around the Me groups.

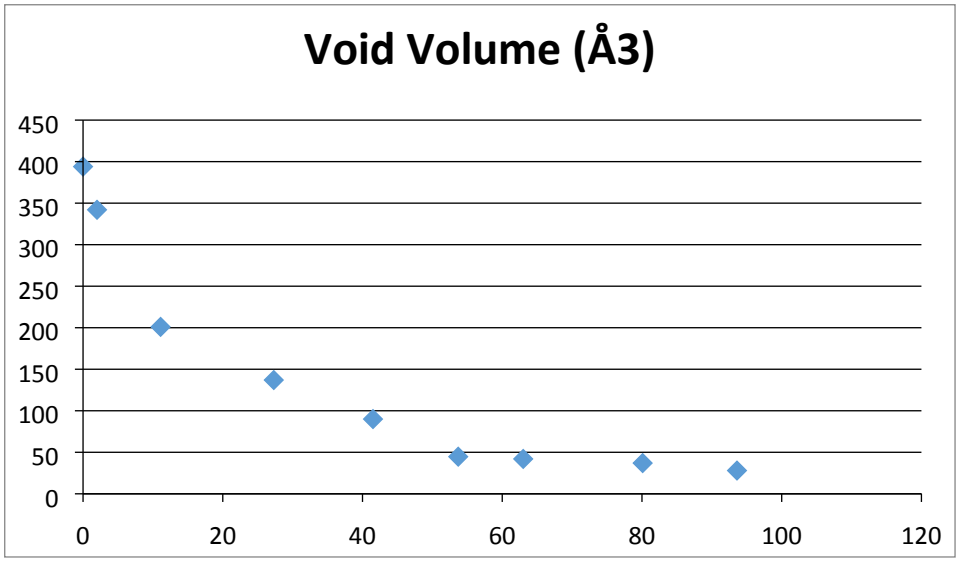


Figure S4: Graph of void volume vs. pressure for **2** (calculated using CrystalExplorer).

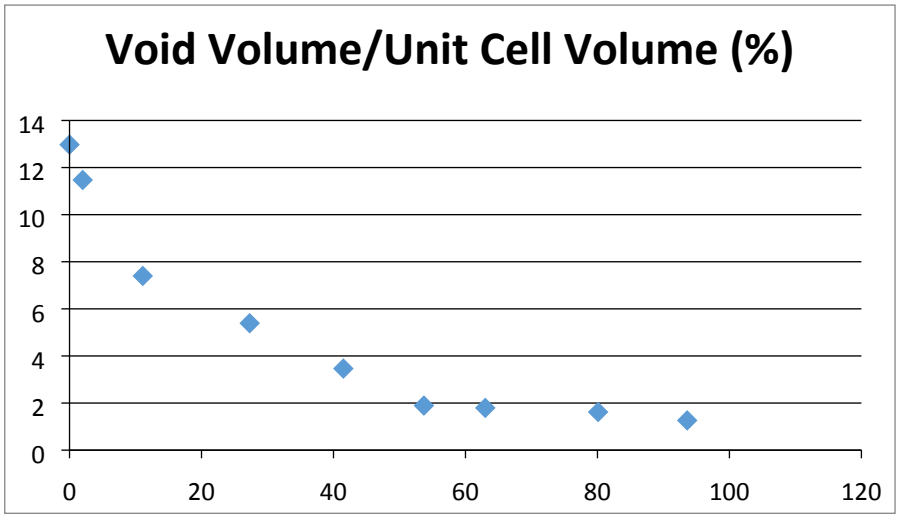


Figure S5: Graph of void volume as a percentage of unit cell volume for **2**