Supporting Information

Ferroelectric Valence Transition and Phase Diagram of a Series of Charge-Transfer Complexes of 4,4'-Dimethyltetrathiafulvalene and Tetrahalo-*p*-benzoquinones

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Abstract. An X-ray crystallographic analysis of a series of DMTTF-QBr_nCl_{4-n} complexes [DMTTF = 4,4'-Dimethyltetrathiafulvalene, QBr_nCl_{4-n} = tetrahalo-*p*-benzoquinone where n (or 4-n) represents the number of Br (or Cl) substituents (n = 0-4)] reveals that the π-electron donor DMTTF and the acceptor QBr_nCl_{4-n} are stacked alternately to form an isomorphous columnar structure. The increment of Br content n in QBr_nCl_{4-n} resulted in the lattice expansion, which is essential for the lowered critical temperature of ferroelectric valence transiton.

Experimental. The intensity data collection for DMTTF-QBr_nCl_{4-n} crystals was performed on a Rigaku AFC7R four-circle diffractometer by using graphite-monochromated MoKα radiation. All the calculations were made on the teXsan crystallographic software package of the Molecular Structure Corporation. The hydrogen atoms were not included in the least-square refinements. The QBr_nCl_{4-n} (n = 1-3) molecules show the orientational disorder with respect to two crystallographycally-independent Cl/Br sites, the occupation of which were determined by population analysis except the 2,6-QBr_2Cl_2 with equal Br/Cl ratios. The final refinements of non-hydrogen atoms were done with anisotropic thermal factors. The final atomic parameters, bond lengths and angles are listed in Tables X1-12, X13 and X14, respectively. The labeling scheme is given in Figure X1.

Figure X1. Atomic numbering schemes of DMTTF and QBr_nCl_{4-n} molecules for the crystal structure.

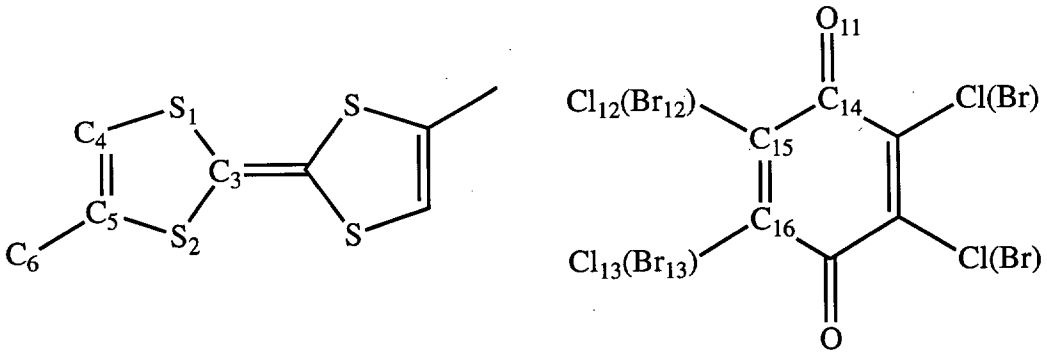

Table X1. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-QCl_4 crystal.

atom	x	y	z	B_{eq}
S(1)	0.23791(7)	0.51871(7)	0.38486(8)	2.95(1)
S(2)	0.41867(7)	0.23798(7)	0.41787(8)	2.85(1)
C(3)	0.4285(2)	0.4491(2)	0.4588(3)	2.35(4)
C(4)	0.1233(3)	0.3253(3)	0.3044(3)	3.12(5)
C(5)	0.2021(3)	0.1979(3)	0.3194(3)	3.00(5)
C(6)	0.1258(4)	0.0242(3)	0.2625(4)	4.69(7)
O(11)	0.2717(2)	0.6981(2)	-0.0688(2)	3.28(4)
Cl(12)	0.12552(7)	0.35784(7)	-0.18310(8)	3.14(1)
Cl(13)	0.40447(8)	0.12150(6)	-0.12182(9)	3.15(1)
C(14)	0.3739(3)	0.6078(2)	-0.0334(3)	2.25(4)
C(15)	0.3326(2)	0.4287(2)	-0.0863(3)	2.11(4)
C(16)	0.4495(3)	0.3283(2)	-0.0598(3)	2.17(4)

$B_{eq}=(3\pi^2/8)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + U_{12}aa^*\ bb^* \cos\gamma + U_{13}aa^*\ cc^* \cos\beta + U_{23}bb^*cc^* \cos\alpha]$

Table X2. Anisotropic thermal parameters for of DMTTF-QCl_4 crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0278(3)	0.0413(3)	0.0422(3)	0.0103(2)	-0.0049(2)	0.0072(3)
S(2)	0.0353(3)	0.0299(3)	0.0417(3)	0.0052(2)	-0.0012(2)	0.0062(2)
C(3)	0.026(1)	0.030(1)	0.033(1)	0.0070(8)	-0.0015(8)	0.0059(9)
C(4)	0.027(1)	0.050(1)	0.037(1)	-0.0003(10)	-0.0018(9)	0.004(1)
C(5)	0.033(1)	0.041(1)	0.035(1)	-0.0049(10)	0.0035(9)	0.0022(10)
C(6)	0.053(2)	0.049(2)	0.066(2)	-0.015(1)	0.003(1)	0.001(1)
O(11)	0.0348(9)	0.0342(8)	0.057(1)	0.0138(7)	-0.0074(7)	0.0115(8)
Cl(12)	0.0266(3)	0.0405(3)	0.0499(4)	0.0012(2)	-0.0089(2)	0.0091(3)
Cl(13)	0.0462(3)	0.0240(3)	0.0484(3)	0.0043(2)	-0.0048(3)	0.0079(2)
C(14)	0.027(1)	0.030(1)	0.031(1)	0.0087(8)	0.0018(8)	0.0092(9)
C(15)	0.0219(10)	0.030(1)	0.028(1)	0.0033(8)	-0.0015(8)	0.0064(8)
C(16)	0.029(1)	0.0235(10)	0.030(1)	0.0032(8)	-0.0003(8)	0.0068(8)

Table X3. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-$QBrCl_3$ crystal.

atom	x	y	z	B_{eq}
S(1)	0.2391(2)	0.5190(2)	0.3852(2)	2.89(3)
S(2)	0.4177(2)	0.2407(2)	0.4132(2)	2.75(3)
C(3)	0.4281(7)	0.4500(7)	0.4572(8)	2.3(1)
C(4)	0.1239(7)	0.3275(8)	0.3028(9)	3.1(1)
C(5)	0.2016(8)	0.2017(8)	0.3150(9)	3.0(1)
C(6)	0.124(1)	0.0261(9)	0.256(1)	4.6(2)
O(11)	0.2696(5)	0.6929(5)	-0.0637(7)	3.26(10)
Br/Cl(12)	0.1211(1)	0.3539(1)	-0.1868(2)	3.63(3)
Br/Cl(13)	0.4069(1)	0.1157(1)	-0.1330(2)	3.73(3)
C(14)	0.3729(7)	0.6060(6)	-0.0316(8)	2.2(1)
C(15)	0.3335(7)	0.4273(6)	-0.0871(8)	2.1(1)
C(16)	0.4516(7)	0.3306(6)	-0.0633(8)	2.1(1)

(*) The occupancy factors of Br in the Br/Cl(12) and Br/Cl(13) sites are 0.181 and 0.319, respectively.

Table X4. Anisotropic thermal parameters for of DMTTF- $QBrCl_3$ crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0252(7)	0.0401(8)	0.0436(9)	0.0099(6)	-0.0067(6)	0.0078(7)
S(2)	0.0322(7)	0.0294(7)	0.0412(9)	0.0050(6)	-0.0036(6)	0.0060(6)
C(3)	0.024(3)	0.030(3)	0.033(3)	0.006(2)	-0.003(2)	0.006(2)
C(4)	0.020(3)	0.054(4)	0.040(3)	-0.003(3)	-0.005(2)	0.005(3)
C(5)	0.031(3)	0.040(3)	0.038(3)	-0.004(2)	0.002(2)	0.004(3)
C(6)	0.053(4)	0.041(4)	0.070(5)	-0.017(3)	-0.004(4)	0.002(4)
O(11)	0.032(2)	0.033(2)	0.060(3)	0.013(2)	-0.009(2)	0.012(2)
Br/Cl(12)	0.0319(6)	0.0472(7)	0.0564(8)	0.0028(5)	-0.0094(5)	0.0118(5)
Br/Cl(13)	0.0511(6)	0.0335(5)	0.0576(7)	0.0066(4)	-0.0054(5)	0.0132(5)
C(14)	0.025(3)	0.028(3)	0.032(3)	0.007(2)	-0.002(2)	0.009(2)
C(15)	0.021(2)	0.029(3)	0.029(3)	0.003(2)	-0.004(2)	0.006(2)
C(16)	0.028(3)	0.020(2)	0.033(3)	0.005(2)	0.000(2)	0.005(2)

Table X5. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-2,5-QBr_2Cl_2 crystal.

atom	x	y	z	B_{eq}
S(1)	0.2404(2)	0.5191(2)	0.3854(2)	2.78(3)
S(2)	0.4164(2)	0.2434(2)	0.4099(2)	2.62(3)
C(3)	0.4284(7)	0.4509(7)	0.4560(8)	2.2(1)
C(4)	0.1238(8)	0.3304(8)	0.3010(9)	2.9(1)
C(5)	0.2012(8)	0.2043(8)	0.3128(8)	2.8(1)
C(6)	0.121(1)	0.0327(9)	0.255(1)	4.5(2)
O(11)	0.2688(5)	0.6888(5)	-0.0619(7)	3.09(10)
Br/Cl(12)	0.1176(1)	0.3502(1)	-0.1901(2)	3.41(2)
Br/Cl(13)	0.4090(1)	0.11265(9)	-0.1416(1)	3.38(2)
C(14)	0.3725(7)	0.6040(6)	-0.0294(8)	2.0(1)
C(15)	0.3331(7)	0.4262(6)	-0.0887(8)	2.1(1)
C(16	0.4519(7)	0.3317(6)	-0.0656(8)	2.0(1)

(*) The occupancy factors of Br in the Br/Cl(12) and Br/Cl(13) sites are 0.329 and 0.671, respectively.

Table X6. Anisotropic thermal parameters for of DMTTF– 2,5-QBr_2Cl_2 crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0270(7)	0.0402(8)	0.0379(8)	0.0106(6)	-0.0038(6)	0.0085(7)
S(2)	0.0328(8)	0.0300(7)	0.0352(8)	0.0045(6)	-0.0013(6)	0.0067(6)
C(3)	0.026(3)	0.030(3)	0.027(3)	0.005(2)	0.002(2)	0.004(2)
C(4)	0.023(3)	0.050(4)	0.033(3)	0.000(3)	-0.002(2)	0.007(3)
C(5)	0.032(3)	0.041(3)	0.026(3)	-0.002(3)	0.003(2)	0.003(3)
C(6)	0.049(4)	0.044(4)	0.064(5)	-0.018(3)	0.002(4)	0.003(4)
O(11)	0.032(2)	0.034(2)	0.054(3)	0.013(2)	-0.007(2)	0.013(2)
Br/Cl(12)	0.0341(6)	0.0459(6)	0.0473(6)	0.0039(4)	-0.0054(4)	0.0100(5)
Br/Cl(13)	0.0485(5)	0.0307(4)	0.0492(5)	0.0061(3)	-0.0023(4)	0.0114(3)
C(14)	0.024(3)	0.028(3)	0.026(3)	0.008(2)	0.001(2)	0.008(2)
C(15)	0.027(3)	0.029(3)	0.024(3)	0.004(2)	0.001(2)	0.008(2)
C(16)	0.026(3)	0.023(2)	0.026(3)	0.005(2)	0.001(2)	0.008(2)

Table X7. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-2,6-QBr_2Cl_2 crystal.

atom	x	y	z	B_{eq}
S(1)	0.2408(1)	0.51998(10)	0.3857(1)	2.97(2)
S(2)	0.4170(1)	0.24321(9)	0.4100(1)	2.84(2)
C(3)	0.4290(4)	0.4505(3)	0.4569(4)	2.43(6)
C(4)	0.1250(4)	0.3315(4)	0.3016(5)	3.04(7)
C(5)	0.2018(4)	0.2053(4)	0.3134(5)	2.98(6)
C(6)	0.1230(5)	0.0341(5)	0.2546(6)	4.64(9)
O(11)	0.2688(3)	0.6894(3)	-0.0623(4)	3.41(5)
Br/Cl(12)	0.11791(6)	0.34918(6)	-0.18933(7)	3.391(9)
Br/Cl(13)	0.40934(7)	0.11381(5)	-0.13950(8)	3.67(1)
C(14)	0.3723(4)	0.6038(3)	-0.0297(4)	2.26(5)
C(15)	0.3341(4)	0.4268(3)	-0.0875(4)	2.20(5)
C(16)	0.4535(4)	0.3307(3)	-0.0648(4)	2.16(5)

(*) The occupancy factors of Br in both Br/Cl(12) and Br/Cl(13) sites are 0.5.

Table X8. Anisotropic thermal parameters for of DMTTF– 2,6-QBr_2Cl_2 crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0276(4)	0.0392(4)	0.0461(5)	0.0103(3)	-0.0051(3)	0.0101(3)
S(2)	0.0342(4)	0.0293(4)	0.0433(4)	0.0050(3)	-0.0025(3)	0.0080(3)
C(3)	0.027(1)	0.030(1)	0.035(2)	0.008(1)	-0.002(1)	0.007(1)
C(4)	0.023(1)	0.050(2)	0.039(2)	-0.001(1)	-0.001(1)	0.008(1)
C(5)	0.031(2)	0.041(2)	0.035(2)	-0.005(1)	-0.001(1)	0.004(1)
C(6)	0.052(2)	0.046(2)	0.069(3)	-0.016(2)	0.001(2)	0.006(2)
O(11)	0.035(1)	0.034(1)	0.064(2)	0.0135(9)	-0.006(1)	0.014(1)
Br/Cl(12)	0.0303(2)	0.0430(2)	0.0535(3)	0.0024(2)	-0.0078(2)	0.0115(2)
Br/Cl(13)	0.0511(3)	0.0308(2)	0.0596(3)	0.0076(2)	-0.0023(2)	0.0152(2)
C(14)	0.029(1)	0.026(1)	0.034(1)	0.007(1)	0.002(1)	0.011(1)
C(15)	0.025(1)	0.027(1)	0.032(1)	0.002(1)	0.000(1)	0.009(1)
C(16)	0.028(1)	0.022(1)	0.032(1)	0.004(1)	0.002(1)	0.007(1)

Table X9. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-QBr_3Cl crystal.

atom	x	y	z	B_{eq}
S(1)	0.2418(1)	0.5201(1)	0.3857(2)	2.96(2)
S(2)	0.4155(1)	0.2454(1)	0.4066(2)	2.79(2)
C(3)	0.4288(5)	0.4506(5)	0.4570(6)	2.45(8)
C(4)	0.1251(5)	0.3340(6)	0.3006(6)	3.00(9)
C(5)	0.2009(6)	0.2068(5)	0.3099(6)	2.97(9)
C(6)	0.1206(7)	0.0400(6)	0.2515(9)	4.6(1)
O(11)	0.2674(4)	0.6858(4)	-0.0601(5)	3.43(7)
Br/Cl(12)	0.11470(7)	0.34710(7)	-0.19316(8)	3.19(1)
Br/Cl(13)	0.41445(7)	0.11306(6)	-0.14541(8)	3.36(1)
C(14)	0.3719(5)	0.6012(5)	-0.0283(6)	2.36(8)
C(15)	0.3347(5)	0.4265(4)	-0.0896(6)	2.12(7)
C(16)	0.4545(5)	0.3314(4)	-0.0670(5)	2.15(7)

(*) The occupancy factors of Br in the Br/Cl(12) and Br/Cl(13) sites are 0.702 and 0.798, respectively.

Table X10. Anisotropic thermal parameters for of DMTTF- QBr_3Cl crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0268(5)	0.0412(6)	0.0443(6)	0.0116(4)	-0.0042(4)	0.0100(5)
S(2)	0.0328(5)	0.0307(5)	0.0410(6)	0.0060(4)	-0.0024(4)	0.0073(4)
C(3)	0.024(2)	0.034(2)	0.034(2)	0.008(2)	-0.001(2)	0.007(2)
C(4)	0.024(2)	0.049(3)	0.038(2)	0.001(2)	0.001(2)	0.008(2)
C(5)	0.030(2)	0.044(2)	0.035(2)	-0.003(2)	0.000(2)	0.007(2)
C(6)	0.051(3)	0.048(3)	0.068(4)	-0.011(2)	-0.001(3)	0.009(3)
O(11)	0.035(2)	0.037(2)	0.061(2)	0.016(1)	-0.005(1)	0.015(2)
Br/Cl(12)	0.0274(3)	0.0430(3)	0.0481(3)	0.0039(2)	-0.0060(2)	0.0099(2)
Br/Cl(13)	0.0464(3)	0.0286(3)	0.0525(3)	0.0072(2)	-0.0034(2)	0.0113(2)
C(14)	0.028(2)	0.030(2)	0.032(2)	0.010(2)	0.000(2)	0.008(2)
C(15)	0.023(2)	0.027(2)	0.031(2)	0.006(1)	0.001(1)	0.008(2)
C(16)	0.026(2)	0.027(2)	0.029(2)	0.006(1)	0.000(2)	0.008(2)

Table X11. Atomic coordinates and equivalent isotropic thermal parameters of DMTTF-QBr_4 crystal.

atom	x	y	z	B_{eq}
S(1)	0.2434(3)	0.5199(2)	0.3856(3)	3.06(5)
S(2)	0.4152(3)	0.2472(2)	0.4040(3)	2.90(5)
C(3)	0.4277(9)	0.4507(8)	0.456(1)	2.5(2)
C(4)	0.126(1)	0.3330(9)	0.299(1)	3.3(2)
C(5)	0.203(1)	0.2095(8)	0.307(1)	3.1(2)
C(6)	0.119(1)	0.0421(10)	0.249(1)	4.8(3)
O(11)	0.2673(7)	0.6826(5)	-0.0558(8)	3.5(1)
Br(12)	0.1125(1)	0.34494(9)	-0.1954(1)	3.03(2)
Br(13)	0.4172(1)	0.11308(8)	-0.1489(1)	3.25(2)
C(14)	0.3710(9)	0.5998(8)	-0.027(1)	2.2(2)
C(15)	0.3337(9)	0.4240(7)	-0.0875(10)	2.2(2)
C(16)	0.4551(10)	0.3336(7)	-0.0680(10)	2.3(2)

Table X12. Anisotropic thermal parameters for of DMTTF-QBr_4 crystal.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.030(1)	0.038(1)	0.049(1)	0.0084(9)	-0.003(1)	0.0147(10)
S(2)	0.037(1)	0.0267(9)	0.046(1)	0.0025(8)	-0.002(1)	0.0116(9)
C(3)	0.027(5)	0.031(4)	0.037(5)	0.005(3)	-0.001(4)	0.013(3)
C(4)	0.030(5)	0.048(5)	0.042(5)	-0.001(4)	-0.004(4)	0.009(4)
C(5)	0.039(5)	0.033(4)	0.041(5)	-0.004(4)	-0.004(4)	0.011(4)
C(6)	0.045(6)	0.047(5)	0.082(8)	-0.019(4)	0.000(6)	0.015(5)
O(11)	0.029(3)	0.032(3)	0.073(4)	0.008(2)	-0.012(3)	0.019(3)
Br(12)	0.0272(5)	0.0372(4)	0.0495(6)	0.0001(3)	-0.0062(4)	0.0131(4)
Br(13)	0.0477(6)	0.0216(4)	0.0554(6)	0.0035(3)	-0.0032(5)	0.0141(4)
C(14)	0.025(4)	0.027(4)	0.033(4)	0.010(3)	0.000(3)	0.010(3)
C(15)	0.024(4)	0.025(3)	0.033(4)	0.005(3)	-0.004(3)	0.009(3)
C(16)	0.034(5)	0.016(3)	0.037(4)	0.001(3)	-0.001(4)	0.006(3)

Table X13. Bond distances (Å) in the series of DMTTF-QBr_nCl_{4-n} crystals.

Br content n in QBr_nCl_{4-n}	0	1	2(2,5)	2(2,6)	3	4
S(1) - C(3)	1.750(2)	1.747(5)	1.742(6)	1.752(3)	1.757(4)	1.745(7)
S(1) - C(4)	1.743(2)	1.746(7)	1.741(7)	1.739(3)	1.735(5)	1.751(8)
S(2) - C(3)	1.745(2)	1.750(6)	1.751(6)	1.745(3)	1.742(4)	1.739(7)
S(2) - C(5)	1.755(2)	1.757(6)	1.749(6)	1.754(3)	1.754(4)	1.738(8)
C(3) - C(3)	1.352(4)	1.36(1)	1.35(1)	1.352(6)	1.354(8)	1.37(1)
C(4) - C(5)	1.321(3)	1.317(9)	1.332(9)	1.327(5)	1.343(6)	1.33(1)
C(5) - C(6)	1.489(3)	1.520(9)	1.509(9)	1.501(5)	1.482(7)	1.50(1)
O(11) - C(14)	1.217(2)	1.208(6)	1.209(6)	1.211(3)	1.221(5)	1.207(7)
Cl/Br(12) - C(15)	1.707(2)	1.757(5)	1.785(6)	1.800(3)	1.834(4)	1.854(7)
Cl/Br(13) - C(16)	1.707(2)	1.792(5)	1.840(5)	1.821(3)	1.847(4)	1.875(6)
C(14) - C(15)	1.479(3)	1.491(7)	1.495(7)	1.488(4)	1.480(5)	1.498(9)
C(14) - C(16)	1.485(3)	1.485(7)	1.487(7)	1.483(4)	1.485(5)	1.487(9)
C(15)- C(16)	1.342(3)	1.335(7)	1.335(7)	1.346(4)	1.355(5)	1.337(9)

Table X14. Bond angles (deg) in the series of DMTTF-QBr_nCl_{4-n} crystals.

Br content n in QBr_nCl_{4-n}	0	1	2(2,5)	2(2,6)	3	4
C(3) - S(1) - C(4)	94.8(1)	94.7(3)	95.1(3)	95.0(2)	94.9(2)	94.5(3)
C(3) - S(2) - C(5)	95.5(1)	95.3(3)	95.6(3)	95.5(2)	96.0(2)	95.5(3)
S(1) - C(3) - S(2)	114.5(1)	114.7(3)	114.5(3)	114.4(2)	114.4(2)	115.0(4)
S(1) - C(3) - C(3)	122.7(2)	123.1(6)	123.4(6)	122.7(3)	122.3(4)	122.5(7)
S(2) - C(3) - C(3)	122.8(2)	122.3(6)	122.0(6)	122.9(3)	123.3(4)	122.5(7)
S(1) - C(4) - C(5)	118.6(2)	118.8(5)	118.5(5)	118.6(2)	118.9(3)	118.0(6)
S(2) - C(5) - C(4)	116.5(2)	116.6(5)	116.3(5)	116.5(2)	115.7(3)	117.0(6)
S(2) - C(5) - C(6)	116.8(2)	116.2(5)	117.1(5)	116.7(3)	117.5(4)	117.7(6)
C(4) - C(5) - C(6)	126.7(2)	127.2(6)	126.6(6)	126.8(3)	126.8(4)	125.2(8)
O(11)- C(14)-C(15)	122.2(2)	122.1(5)	121.6(5)	121.9(3)	121.7(4)	122.1(7)
O(11)- C(14)-C(16)	121.6(2)	122.4(5)	122.5(5)	121.9(3)	121.5(4)	121.8(6)
C(15)- C(14)-C(16)	116.2(2)	115.5(4)	115.9(4)	116.2(2)	116.8(3)	116.1(5)
Cl/Br(12)-C(15)-C(14)	115.5(1)	115.1(4)	115.6(4)	115.8(2)	115.8(3)	115.0(5)
Cl/Br(12)-C(15)-C(16)	122.1(2)	122.6(4)	122.6(4)	122.1(2)	122.1(3)	123.7(5)
C(14)- C(15)-C(16)	122.4(2)	122.3(5)	121.7(5)	122.1(3)	122.1(3)	121.2(6)
Cl/Br(13)-C(16)-C(14)	115.6(1)	115.1(4)	114.9(4)	115.9(2)	115.5(3)	114.5(5)
Cl/Br(13)-C(16)-C(15)	123.0(2)	122.7(4)	122.8(4)	122.5(2)	123.4(3)	122.9(6)
C(14)- C(16)-C(15)	121.4(2)	122.2(5)	122.3(5)	121.6(2)	121.1(3)	122.6(6)