Supporting Information

Exploring Hypervalency and Three-Centre, Four-Electron Bonding Interactions: Reactions of Acenaphthene Chalcogen Donors and Dihalogen Acceptors

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1. Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(Se) and δ(Te) referenced to external dimethylselenide and diphenyl ditelluride respectively. Assignments of ^{13}C and ^{1}H NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) was carried out on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer.

[Acenap(SePhI$_2$)(Br)] (1): A solution of 5-bromo-6-(phenylselenyl)acenaphthene (0.193 g, 0.497 mmol) in dichloromethane (5 mL) was treated with iodine (0.126 g, 0.497 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.3 g, 82 %); mp 115-117 ºC; elemental analysis (Found C, 34.1; H, 1.6. Calc. for $C_{18}H_{13}BrI_2Se$: C, 33.7; H, 2.0 %); IR (KBr disk): ν_{max} cm^{-1} 2934w, 1950w, 1860w, 1647w, 1598w, 1573w, 1472s, 1435s, 1419w, 1408w, 1346w, 1323s, 1253w, 1231w, 1210w, 1199w, 1176w, 1116w, 1102w, 1064w, 1019s, 998s, 936w, 854w, 834vs, 809s, 739vs, 702w, 686s, 666w, 600s, 541w, 501w, 472w, 463s, 314w; δ_H(270 MHz, $CDCl_3$, 25 ºC, Me_4Si) 7.68 (1 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 4-H), 7.63-7.55 (2 H, m, Se*Ph* 12,16-H), 7.38-7.27 (3 H, m, Se*Ph* 13-15-H), 7.20 (1 H, d, $^{3}J_{HH}$ 7.5 Hz, Acenap 7-H), 7.07 (1 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 3-H), 6.98 (1 H, d, $^{3}J_{HH}$ 7.5 Hz, Acenap 8-H), 3.30-3.20 (4 H, m, 2 x C*H*$_2$); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 147.6(q), 147.4(q), 142.4(q), 135.6(s), 135.1(s), 134.1(s), 130.4(s), 130.3(q), 129.4(s), 125.7(q), 121.4(s), 121.3(s), 118.5(q), 115.3(q), 30.5(s, *C*H$_2$), 30.4(s, *C*H$_2$); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 437.6(s); MS (ES$^+$): *m/z* 308.94 (M$^+$+H-Br-I$_2$, 100 %), 387.82 (M$^+$+H-I$_2$, 10).

[{Acenap(SePhBr)(SePh)}$^{+}${Br$_{3}$}$^{-}${Br$_{2}$}] (2): A solution of 5,6-bis(phenylselanyl)acenaphthene (0.251 g, 0.541 mmol) in dichloromethane (20 mL) was treated with bromine (0.346 g, 0.11 mL, 2.162 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.3 g, 62 %); mp 68-70 ºC; IR (KBr disk): ν_{max} cm^{-1} 2938w, 2909w, 2857w, 2814w, 2597w, 1959w, 1901w, 1808w, 1751w, 1680w, 1588s, 1573s, 1473s, 1436s, 1410s, 1348s, 1306w, 1264s, 1230w, 1214s, 1176s, 1159w, 1142w, 1103w, 1067w, 1049w, 1021w, 996s, 960w, 948w, 903w, 870w, 848vs, 816s, 727vs, 704s, 677vs, 612s, 594s, 534w, 496w, 454s, 375w, 343s, 304w; δ_{H}(270 MHz; (CD$_3$)$_2$CO; 25 ºC; Me$_4$Si) 7.54 (2 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 4,7-H), 7.47-7.37 (4 H, m, Se*Ph* 12,16,18,22-H), 7.37-7.26 (6 H, m, Se*Ph* 13-15,19-21-H), 7.21 (2 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 3,8-H) 3.37 (4 H, s, 2 x CH_2); δ_{C}(67.9 MHz; (CD$_3$)$_2$CO; 25 ºC; Me$_4$Si) 198.3(q), 154.4(q), 148.4(q), 137.4(s), 135.2(q) 133.9(s), 130.4(s), 128.3(s), 125.9(q), 121.6(s), 30.5(s, 2 x *C*H$_2$); δ_{Se}(51.5 MHz; (CD$_3$)$_2$CO; 25 ºC; PhSeSePh) 405.2 (s); MS (ES$^+$): *m/z* 465.81 (M$^+$-Br$_6$, 100 %), 496.83 (M$^+$+OMe-Br$_6$, 90).

[{Acenap(SePhBr)(SPh)}$^{+}${Br$_{3}$}$^{-}$] (3): A solution of 5-(phenylselanyl)-6-(phenylsulfanyl)acenaphthene (0.110 g, 0.264 mmol) in dichloromethane (20 mL) was treated with bromine (0.084 g, 0.03 mL, 0.527 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.1 g, 60 %); mp 80-82 ºC; IR (KBr disk): ν_{max} cm^{-1} 2921w, 1890w, 1719w, 1655w, 1589s, 1473s, 1440s, 1411w, 1386w, 1351s, 1336s, 1262w, 1233w, 1215w, 1181w, 1161w, 1109w, 1068w, 1051w, 1022w, 1006w, 995s, 918w, 850w, 812w, 734vs, 678s, 619w, 598w, 547w, 476w, 459s, 405w, 341w, 319w; δ_{H}(270 MHz; (CD$_3$)$_2$CO; 25 ºC; Me$_4$Si) 7.68 (1 H, d, $^{3}J_{HH}$ 7.3 Hz, Acenap 4-H), 7.47-7.40 (2 H, m, Se*Ph* 12,16-H), 7.33-7.24 (4 H, m, Acenap 3-H, Se*Ph* 13-15-H), 7.15-7.09 (2 H, m, S*Ph* 18,22-H) 7.05-6.94 (5 H, m, Acenap 7,8-H, S*Ph* 19-21-H), 3.35-3.26 (2 H, m, CH_2), 3.26-3.17 (2 H, m, CH_2); δ_{C}(67.9 MHz; (CD$_3$)$_2$CO; 25 ºC; Me$_4$Si) 154.7(q), 151.2(q), 146.8(q), 141.3(s), 137.4(s), 137.3(q), 133.2(q), 133.0(s), 131.0(s), 130.2(s), 129.8(q), 129.7(s), 128.7(q), 128.4(s), 126.8(s), 125.8(q), 122.1(s), 121.8(s), 31.3(s, *C*H$_2$), 30.7(s, *C*H$_2$); δ_{Se}(51.5 MHz; (CD$_3$)$_2$CO; 25 ºC; PhSeSePh) 431.2 (s); MS (ES$^+$): *m/z* 417.84 (M$^+$+H-Br$_4$, 100 %), 448.93 (M$^+$+OMe-Br$_4$, 20), 495.82 (M$^+$-Br$_3$, 10).

[Acenap(SePhI$_2$)(SePh)] (4): A solution of 5,6-bis(phenylselanyl)acenaphthene (0.212 g, 0.457 mmol) in dichloromethane (20 mL) was treated with iodine (0.116 g, 0.457 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.2 g, 71 %); mp 92-94 ºC; elemental analysis (Found: C, 40.4; H, 2.7. Calc. for $C_{24}H_{18}I_2Se_2$: C, 40.1; H, 2.5 %); IR (KBr disk): ν_{max} cm^{-1} 3140w, 3039s, 2987w, 2929s, 2850w, 2810w, 2628w, 2580w, 2532w, 2422w, 2338w, 2237w, 2163w, 2121w, 1958w, 1882s, 1805w, 1754w, 1659w, 1593s, 1572s, 1471s, 1433s, 1406s, 1359w, 1319s, 1301s, 1254w, 1230w, 1205s, 1176s, 1155w, 1114w, 1103s, 1063s, 1018s, 996s, 972w, 919w, 904w, 838vs, 811s, 774s, 739vs, 687s, 663s, 600s, 542w, 499w, 455s, 337w, 313w; δ_{H}(270 MHz; CDCl$_3$; 25 ºC; Me$_4$Si) 7.64 (2 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 4,7-H), 7.50-7.41 (4 H, m, Se*Ph* 12,16,18,22-H), 7.35-7.25 (6 H, m, Se*Ph* 13-15,19-21-H), 7.21 (2 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 3,8-H) 3.41 (4 H, s, 2 x CH_2); δ_{C}(67.9 MHz; CDCl$_3$; 25 ºC; Me$_4$Si) 148.7(q), 141.8(q), 137.9(s), 135.1(q), 134.3(q), 133.5(q), 133.1(s), 131.0(q), 130.0(s), 128.2(s), 127.0(q), 124.5(q), 121.3(s), 30.6(s, 2 x *C*H$_2$); δ_{Se}(51.5 MHz; CDCl$_3$; 25 ºC; PhSeSePh) 421.0 (s); MS (ES$^+$): *m/z* 465.84 (M$^+$+H-I$_2$, 100 %), 496.89 (M$^+$+OMe-I$_2$, 40).

[Acenap(SePhI$_2$)(SPh)] (5): A solution of 5-(phenylselanyl)-6-(phenylsulfanyl)acenaphthene (0.214 g, 0.513 mmol) in dichloromethane (20 mL) was treated with iodine (0.130 g, 0.513 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.3 g, 82 %); mp 60-62 ºC; elemental analysis (Found: C, 43.0; H, 2.7. Calc. for $C_{24}H_{18}I_2SSe$: C, 42.9; H, 2.7 %); IR (KBr disk): ν_{max} cm^{-1} 2919w, 1882w, 1595s, 1576s, 1474s, 1436s, 1409w, 1360w, 1322s, 1300w, 1207w, 1177w, 1156w, 1108w, 1066w, 1022s, 998s, 903w, 866w, 841s, 814w, 773w, 742vs, 689vs, 666w, 625w, 605w, 475w, 460w, 403w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.90 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 7.72-7.62 (2 H, m, Se*Ph* 12,16-H), 7.46-7.36 (4 H, m, Acenap 3-H, Se*Ph* 13-15-H), 7.28-7.19 (3 H, m, Acenap 7-H, S*Ph* 19,21-H), 7.18-7.09 (2 H, m, Acenap 8-H, S*Ph* 20-H), 7.09-7.01 (2 H, m, S*Ph* 18,22-H), 3.53-3.43 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 148.1(q), 142.0(q), 141.3(s), 140.6(q), 136.9(q), 135.7(s), 133.5(s), 132.9(q), 131.4(q), 130.4(s), 129.8(s), 129.5(s), 128.1(q), 127.3(s), 126.0(s), 124.2(q), 121.4(s), 121.3(s), 31.0(s, CH_2), 30.5(s, CH_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 460.4 (s); MS (ES$^+$): *m/z* 417.90 (M^++H-I_2, 100 %).

[Acenap(TePhBr$_2$)(Br)] (6): A solution of 5-bromo-6-(phenyltelluro)acenaphthene (0.124 g, 0.284 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.284 mmol, 2.84 mL). The mixture was stirred at room temperature for 2 h after which time a yellow precipitate had formed which was collected by filtration and washed with dichloromethane. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.1 g, 34 %); mp 250-252ºC; elemental analysis (Found: C, 36.4; H, 1.7 Calc. for $C_{18}H_{13}Br_3Te$: C, 36.2; H, 2.2 %); IR (KBr disk): ν_{max} cm^{-1} 2924w, 2905w, 1654w, 1595s, 1566w, 1472w, 1431s, 1415s, 1346w, 1328s, 1258w, 1228w, 1209w, 1183s, 1102w, 1067w, 1045w, 1015w, 993w, 972w, 944w, 913w, 838vs, 813s, 741vs, 686s, 595w, 536w, 491w, 458w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.53-8.42 (2 H, m, Te*Ph* 12,16-H), 7.89 (1 H, d, $^3J_{HH}$ 7.6 Hz, Acenap 4-H), 7.84 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 7-H), 7.62-7.48 (3 H, m, Te*Ph* 13-15-H), 7.24 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 8-H), 7.22-7.18 (1 H, m, Acenap 3-H), 3.44-3.28 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 152.8(q), 148.3(q), 142.4(q), 137.9(s), 137.7(s), 135.6(s), 132.2(s), 130.5(s), 130.4(q), 129.5(q), 128.5(q), 122.4(s), 121.8(s), 115.4(q), 31.0(s, CH_2), 30.5(s, CH_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 918.8; MS (ES$^+$): *m/z* 468.79 (M^+-I_2+OMe, 100 %).

[Acenap(TePhI$_2$)(Br)] (7): A solution of 5-bromo-6-(phenyltelluro)acenaphthene (0.128 g, 0.293 mmol) in dichloromethane (10 mL) was treated with iodine (0.074 g, 0.293 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.2 g, 79 %); mp 208-210ºC; elemental analysis (Found C, 31.6; H, 1.5 Calc. for $C_{18}H_{13}BrI_2Te$: C, 31.3; H, 1.9 %); IR (KBr disk): ν_{max} cm^{-1} 2914w, 2819w, 1876w, 1867w, 1704w, 1656w, 1594vs, 1573s, 1483s, 1469s, 1445s, 1433vs, 1415s, 1348w, 1326vs, 1258s, 1232s, 1213s, 1183s, 1159s, 1105s, 1045s, 1015w, 993s, 920w, 837vs, 809vs, 737vs, 702s, 683s, 593s, 534s, 489w, 449s, 309w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.54-8.45 (2 H, m, Te*Ph* 12,16-H), 7.93 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 4-H), 7.83 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 7-H), 7.62-7.54 (1 H, m, Te*Ph* 14-H), 7.48-7.40 (2 H, m, Te*Ph* 13,15-H), 7.24 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 8-H), 7.11 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 3-H), 3.40-3.28 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 152.6(q), 148.4(q), 146.5(q), 142.7(q), 140.2(s), 138.8(s), 135.6(s), 135.4(q), 132.1(s), 130.7(s), 129.8(q), 122.5(s), 122.1(s), 115.5(q), 31.0(s, CH_2), 30.5(s, CH_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 860.6; MS (ES$^+$): *m/z* 468.78 (M^+-Br_2+OMe, 100 %).

[Acenap(TePhBr$_2$)(SPh)] (8): A solution of 5-(phenyltelluro)-6-(phenylsulfanyl)acenaphthene (0.181 g, 0.3883 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.3883 mmol, 3.9 mL). The mixture was stirred at room temperature for 2 h and the solvent removed *in vacuo*. The crude product was washed with diethyl ether and the yellow precipitate which formed was collected by filtration. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.1 g, 50 %); mp 188-190ºC; elemental analysis (Found C, 46.2; H, 2.2 Calc. for $C_{24}H_{18}Br_2STe$: C, 46.1; H, 2.9 %); IR (KBr disk): ν_{max} cm^{-1} 2986w, 2944w, 2915w, 2820w, 2777w, 2697w, 2643w, 2546w, 2523w, 2429w, 2363w, 2321w, 2206w, 2159w, 2047w, 1947w, 1876w, 1796w, 1638w, 1589s, 1572s, 1472s, 1433vs, 1414w, 1331vs, 1256w, 1230w, 1207w, 1177w, 1157w, 1101w, 1067w, 1050w, 1021w, 995w, 952w, 917w, 846s, 815w, 745vs, 730vs, 697s, 684s, 623w, 602w, 577w, 549w, 510w, 491w, 450w, 411w, 371w, 326w, 305w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.48-8.38 (2 H, m, *Te*Ph 12,16-H), 8.04 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 4-H), 8.01 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 7-H), 7.65-7.52 (3 H, m, Te*Ph* 13-15-H), 7.50 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 3-H), 7.36 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 8-H), 7.30-7.12 (5 H, m, Se*Ph* 18-22-H), 3.57-3.46 (4 H, m, 2 x C*H*$_2$); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 152.6(q), 151.0(q), 143.4(q), 141.7(s), 139.8(q), 138.5(s), 137.6(q), 137.5(s), 134.2(q), 131.7(s), 130.2(s), 129.7(s), 129.1(q), 128.3(s), 127.2(s), 123.9(q), 122.1(s), 121.9(s), 31.0(s, *C*H$_2$), 30.9(s, *C*H$_2$); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 930.6; MS (ES$^+$): *m/z* 498.93 (M$^+$+OMe-Br$_2$, 100 %).

[Acenap(TePhBr$_2$)(SePh)] (9): A solution of 5-(phenyltelluro)-6-(phenylselanyl)acenaphthene (0.095 g, 0.1851 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.1851 mmol, 1.85 mL). The mixture was stirred at room temperature for 2 h and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.1 g, 86 %); mp 188-190ºC; elemental analysis (Found: C, 43.3; H, 1.9 Calc. for $C_{24}H_{18}Br_2SeTe$: C, 42.8; H, 2.7 %); IR (KBr disk): ν_{max} cm^{-1} 2919w, 2853w, 1952w, 1888w, 1706w, 1654w, 1640w, 1590s, 1571s, 1472s, 1433s, 1384w, 1328s, 1254w, 1228w, 1178w, 1097w, 1062w, 1048w, 1017w, 996w, 915w, 843s, 811s, 731vs, 684s, 614w, 598w, 534w, 479w, 449s; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.33-8.22 (2 H, m, *Te*Ph 12,16-H), 8.06 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 7.94 (1 H, d, $^3J_{HH}$ 7.6 Hz, Acenap 7-H), 7.51-7.40 (3 H, m, Te*Ph* 13,15-H), 7.32 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 3-H), 7.28-7.20 (3 H, m, Acenap 8-H, Se*Ph* 18,22-H), 7.14-7.05 (3 H, m, Se*Ph* 19-21-H), 3.39 (4 H, br s, 2 x C*H*$_2$); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 152.8(q), 150.8(q), 143.0(s), 141.7(q), 139.4(s), 137.3(s), 135.5(q), 135.0(q), 133.9(q), 132.3(q), 131.9(s), 131.6(s), 130.9(s), 130.2(s), 129.9(s), 127.8(s), 122.6(q), 122.2(s), 121.7(s), 30.9(s, *C*H$_2$), 30.8(s, *C*H$_2$); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 332.9 (s); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 921.9; MS (ES$^+$): *m/z* 544.79 (M$^+$ -Br$_2$+OMe, 100 %).

[Acenap(TePhI$_2$)(SPh)] (10): A solution of 5-(phenyltelluro)-6-(phenylsulfanyl)acenaphthene (0.208 g, 0.446 mmol) in dichloromethane (20 mL) was treated with iodine (0.113 g, 0.446 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.253 g, 77 %); mp 177-179 ºC; elemental analysis (Found C, 39.7; H, 1.5 Calc. for $C_{24}H_{18}TeSI_2$: C, 40.0; H, 2.5 %); IR (KBr disk): ν_{max} cm^{-1} 2905w, 2824w, 1592s, 1569s, 1473s, 1434s, 1417s, 1331s, 1258w, 1232w, 1209w, 1177w, 1152w, 1105w, 1067w, 1050w, 1022w, 995s, 944w, 913w, 896w, 846s, 813s, 732vs, 686s, 626w, 603w, 581w, 548w, 484w, 452s, 404w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.38 (2 H, m, Te*Ph* 12,16-H), 8.02 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 4-H), 7.95 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 7-H), 7.55-7.45 (1 H, m, Te*Ph*

14-H), 7.45-7.32 (3 H, m, Acenap 8-H, Te*Ph* 13,15-H), 7.28 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 3-H), 7.17-7.06 (3 H, m, S*Ph* 19-21-H), 7.06-6.97 (2 H, m, S*Ph* 18,22-H), 3.47-3.35 (4 H, s, 2 x C*H*$_2$); δ_C(67.9 MHz; CDCl$_3$; 25 ºC; Me$_4$Si) 152.6(q), 151.2(q), 141.6(s), 139.8(q), 139.3(q), 131.6(s), 130.3(s), 129.8(s), 129.4(q), 128.3(s), 127.2(s), 126.6(q), 125.1(q), 123.0(q), 122.4(s), 122.3(s), 118.4(q), 114.7(q), 31.1(s, *C*H$_2$), 31.0(s, *C*H$_2$); δ_{Te}(81.2 MHz; CDCl$_3$; 25 ºC; PhTeTePh) 878.9; MS (ES$^+$): *m/z* 498.89 (M$^+$+OMe-I$_2$, 100 %).

[Acenap(TePhI$_2$)(SePh)] (11): A solution of 5-(phenyltelluro)-6-(phenylselanyl)acenaphthene (0.078 g, 0.152 mmol) in dichloromethane (5 mL) was treated with iodine (0.039 g, 0.152 mmol). The mixture was stirred at room temperature for 2 h, filtered and the solvent removed *in vacuo*. An analytically pure sample was obtained by recrystallization from diffusion of hexane into a dichloromethane solution of the product (0.085 g, 73 %); mp 172-174ºC; elemental analysis (Found: C, 37.5; H, 2.3 Calc. for C$_{24}$H$_{18}$TeSeI$_2$: C, 37.6; H, 2.4 %); IR (KBr disk): ν_{max} cm^{-1} 2914w, 1879w, 1711s, 1656w, 1640w, 1592s, 1569s, 1473s, 1431s, 1330s, 1299w, 1258w, 1209s, 1178w, 1154w, 1114w, 1097w, 1067w, 1048w, 1019w, 996s, 913w, 841vs, 811s, 733vs, 683s, 664w, 614w, 595w, 527w, 475w, 454s; δ_H(270 MHz; CDCl$_3$; 25 ºC; Me$_4$Si) 8.36-8.26 (2 H, m, Te*Ph* 12,16-H), 8.07 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 8.06 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 7-H), 7.53-7.44 (1 H, m, Te*Ph* 14-H), 7.41-7.30 (3 H, m, Acenap 3-H, Te*Ph* 13,15-H), 7.23 (1 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 8-H), 7.21-7.15 (2 H, m, Se*Ph* 18,22-H), 7.13-7.06 (3 H, m, Se*Ph* 19-21-H), 3.43-3.31 (4 H, m, 2 x C*H*$_2$); δ_C(67.9 MHz; CDCl$_3$; 25 ºC; Me$_4$Si) 207.4(q), 152.6(q), 150.9(q), 144.8(q), 142.9(s), 141.9(q), 140.7(s), 139.5(s), 134.6(q), 132.9(q), 131.5(s), 130.9(s), 130.3(s), 129.9(s), 127.7(s), 122.5(s), 122.4(q), 122.2(s), 31.4(s, *C*H$_2$), 30.9(s, *C*H$_2$); δ_{Se}(51.5 MHz; CDCl$_3$; 25 ºC; PhSeSePh) 343.2 (s); δ_{Te}(81.2 MHz; CDCl$_3$; 25 ºC; PhTeTePh) 871.0(s); MS (ES$^+$): *m/z* 542.87 (M$^+$-I$_2$+OMe, 100 %).

[Acenap(BrTePh)$_2$O] (12): A solution of 5,6-bis(phenyltelluro)acenaphthene (0.182 g, 0.324 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.324 mmol, 3.3 mL). The mixture was stirred at room temperature for 2 h and the solvent removed *in vacuo*. The crude product was washed with diethyl ether and the yellow precipitate which formed was collected by filtration. An analytically pure sample was obtained by recrystallization from dimethylformamide (0.230 g, 96 %); mp 213-215 ºC; elemental analysis (Found: C, 39.5; H, 2.3 Calc. for C$_{24}$H$_{18}$Br$_2$OTe$_2$: C, 39.1; H, 2.5 %); IR (KBr disk): ν_{max} cm^{-1} 2969w, 2922w, 2870w, 2365w, 2356w, 2331w, 2218w, 2092w, 1880w, 1654w, 1599s, 1592s, 1567s, 1552w, 1483w, 1472s, 1450w, 1433vs, 1413s, 1379w, 1342w, 1329w, 1314vs, 1259w, 1232w, 1218w, 1178w, 1146w, 1105vs, 1048s, 1011w, 994vs, 962w, 932w, 914w, 840vs, 811s, 801s, 731vs, 695w, 681vs, 650w, 610w, 592w, 569w, 535w, 453s; δ_H(270 MHz; (CD$_3$)$_2$NCOD; 25 ºC; Me$_4$Si) 9.18 (2 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 4,7-H), 8.40-8.25 (4 H, m, Te*Ph* 12,16,18,22-H), 7.89-7.75 (8 H, m, Acenap 3,8-H, Te*Ph* 13-15, 19-21-H), 3.81 (4 H, s, 2 x C*H*$_2$); δ_C(67.9 MHz; (CD$_3$)$_2$NCOD; 25 ºC; Me$_4$Si) 152.9(q), 142.9(q), 141.7(q), 141.2(s), 137.1(q), 134.6(s), 132.1(s), 130.7(q), 130.2(s), 129.9(q), 127.2(q), 122.2(q), 121.7(s), 30.8(s, 2 x *C*H$_2$); δ_{Te}(81.2 MHz; (CD$_3$)$_2$NCOD; 25 ºC; PhTeTePh) 961.3(s); MS (ES$^+$): *m/z* 608.73 (M$^+$+OMe-Br$_2$, 100 %).

2. Computational Details

Essentially the same methods and basis sets as in our previous study on per-substituted naphthalenes[1] have been employed. Geometries were fully optimised in the gas phase at the B3LYP level[2] using Curtis and Binning's 962(d) basis[3] on Se and Br (augmented with a set of diffuse s and p functions on Br), the Stuttgart-Dresden effective core potentials along with their double zeta valence basis sets for Te[4] (augmented with a set of d-polarisation functions with exponents of 0.237),[5] and 6-

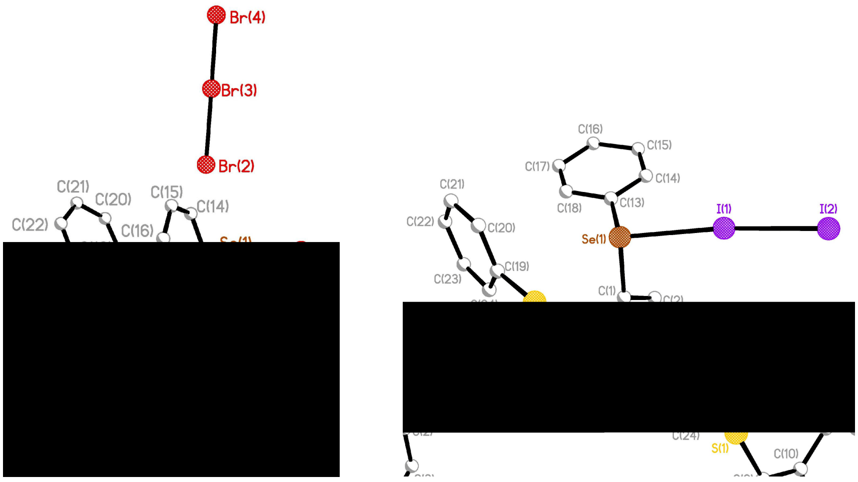
31+G(d) basis elsewhere. Wiberg bond indices[6] were obtained in a natural bond orbital analysis[7] at the same level. The optimisations were started from the experimental structures available from X-ray crystallography, substituting chalcogens and halogens where necessary, and deleting solvent and excess Br_2 molecules if present.

Additional single-point energy calculations were performed using the polarisable continuum model (PCM) of Tomasi and coworkers,[8] employing the same basis sets on Te and Br as before, and 6-311+G(d) elsewhere, together with the parameters of CH_2Cl_2 as a typical solvent. The resulting changes in relative energies were added as increments to the gas-phase free energies, affording the $\Delta G_r(CH_2Cl_2)$ values in Table 5. Empirical dispersion corrections using Grimme's three-body terms[9] have been evaluated for the B3LYP-optimised geometries and added as increments to the $\Delta G_r(CH_2Cl_2)$ values (denoted B3LYP-D3).

Results for (**12**)$_2$ are reported for a structure that was optimised imposing C_2 symmetry. A C_1-symmetris form was indicated to be more stable by ca. 0.3 kcal/mol, but was difficult to converge. Basis-set superposition error for dimerisation of **12** was found to be 3.4 kcal/mol, according to the Counterpoise method.[10] All computations were performed using the Gaussian 03 suite of programs.[11]

3. Crystal structure analyses

X-ray crystal structures for **2**, **4**, **6**, **7**, **9** and **11** were determined at -148(1) °C on the St Andrews Robotic Diffractometer[12] a Rigaku ACTOR-SM, Saturn 724 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data was corrected for Lorentz, polarisation and absorption. Data for compounds **1**, **5**, **8** and **10** were collected at -148(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Saturn CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz, polarisation and absorption. Data for compound **12** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Data for compound **3** were collected at -148(1) °C on a Rigaku SCXmini CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz, polarisation and absorption. The data for the complexes was collected and processed using CrystalClear (Rigaku).[13] The structures were solved by Patterson or direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure[14] and SHELXL-97.[15] These X-ray data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk CCDC Nos:



[redacted]

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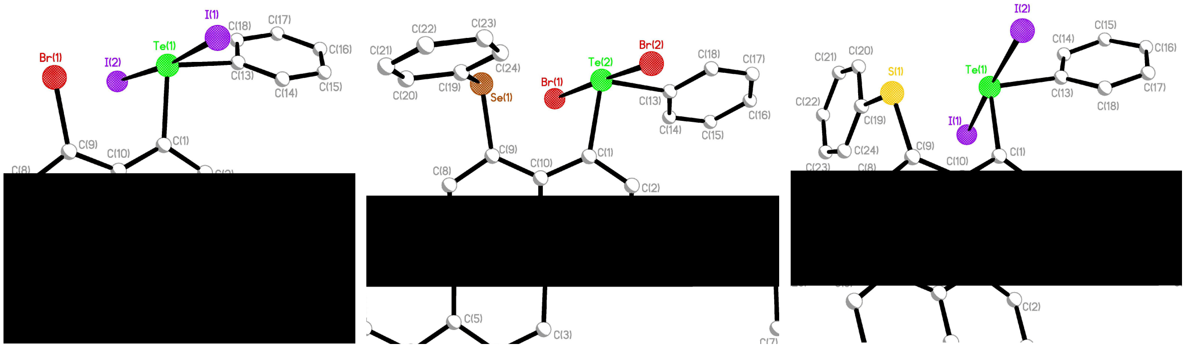
Fig. S1 Molecular structures of **3** and **5** (H atoms omitted for clarity).



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[redacted]

Fig. S2 Molecular structures of **7**, **9** and **10** (H atoms omitted for clarity).

Table S1 Selected interatomic distances [Å] and angles [°] for adducts **1-6** [values in parentheses are for independent molecules].

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Peri moieties	Br $SePhI_2$	BrSePh SePh	BrSePh SPh	I_2SePh SePh	I_2SePh SPh	Br $TePhBr_2$
Peri-region distances and sub-van der Waals contacts						
E(1)···X/E	3.1753(19)	2.801(3)	2.740(3)	3.326(3)	3.252(2)	3.2581(19)
Σr_{vdW} - E···X/E; % ΣrvdW[a]	0.5747; 85	0.999; 74	0.9600; 74	0.474; 88	0.448; 88	0.6519; 83
E(1)-C(1)	1.954(12)	1.97(3)	1.949(9)	1.985(15)	1.949(7)	2.141(13)
X/E-C(9)	1.920(13)	1.90(2)	1.788(10)	1.922(14)	1.803(7)	1.915(14)
Acenaphthene bond lengths						
C(1)-C(2)	1.382(18)	1.37(3)	1.418(11)	1.40(2)	1.387(9)	1.40(2)
C(2)-C(3)	1.391(18)	1.43(4)	1.386(14)	1.37(2)	1.398(10)	1.41(2)
C(3)-C(4)	1.346(17)	1.32(4)	1.393(10)	1.35(2)	1.381(11)	1.401(19)
C(4)-C(5)	1.374(18)	1.47(3)	1.433(11)	1.44(2)	1.418(9)	1.41(2)
C(5)-C(10)	1.452(17)	1.47(3)	1.409(13)	1.416(20)	1.431(9)	1.427(19)
C(5)-C(6)	1.394(16)	1.37(3)	1.411(11)	1.44(2)	1.406(10)	1.416(18)
C(6)-C(7)	1.377(19)	1.33(3)	1.389(12)	1.38(2)	1.376(10)	1.40(2)
C(7)-C(8)	1.418(19)	1.46(3)	1.398(15)	1.36(2)	1.410(10)	1.42(2)
C(8)-C(9)	1.359(16)	1.40(3)	1.406(11)	1.42(2)	1.388(11)	1.361(19)
C(9)-C(10)	1.418(17)	1.38(3)	1.425(10)	1.44(2)	1.446(9)	1.452(20)

C(10)-C(1)	1.419(15)	1.39(3)	1.396(9)	1.42(2)	1.416(10)	1.438(18)
C(4)-C(11)	1.521(17)	1.53(4)	1.504(11)	1.51(2)	1.491(10)	1.506(19)
C(11)-C(12)	1.556(18)	1.57(3)	1.537(11)	1.57(2)	1.551(11)	1.59(2)
C(12)-C(6)	1.518(18)	1.55(3)	1.526(15)	1.50(2)	1.517(9)	1.49(2)
Peri-region bond angles						
E(1)-C(1)-C(10)	122.3(9)	117.2(14)	118.0(6)	122.6(11)	123.4(5)	122.8(10)
C(1)-C(10)-C(9)	133.6(11)	132(2)	129.5(8)	132.6(13)	132.5(6)	132.0(12)
X/E-C(9)-C(10)	120.8(9)	118.1(15)	117.9(6)	125.3(11)	123.1(6)	120.0(9)
Σ of bay angles	376.7(24)	367.3(39)	365.4(16)	380.5(29)	379.0(14)	374.8(25)
Splay angle[b]	16.7	7.3	5.4	20.5	19.0	14.8
C(4)-C(5)-C(6)	111.9(11)	114.3(19)	111.4(8)	110.2(13)	110.6(6)	111.1(12)
Out-of-plane displacement						
E(1)	0.125(1)	-0.073(1)	0.069(1)	-0.091(1)	0.130(1)	0.531(1)
X/E(1)	-0.101(1)	0.121(1)	-0.163(1)	0.179(1)	-0.133(1)	-0.205(1)
Central acenaphthene ring torsion angles						
C:(6)-(5)-(10)-(1)	178.85(1)	179.29(1)	-178.60(1)	-179.55(1)	178.01(1)	174.62(1)
C:(4)-(5)-(10)-(9)	179.14(1)	-176.49(1)	177.79(1)	-178.75(1)	178.30(1)	-179.67(1)

[a] van der Waals radii used for calculations: r_{vdW}(S) 1.80Å, r_{vdW}(Se) 1.90Å, r_{vdW}(Te) 2.06Å, r_{vdW}(Br) 1.85 Å, r_{vdW}(I) 1.98 Å;[16] [b] Splay angle: Σ of the three bay region angles – 360.

Table S2 Selected interatomic distances [Å] and angles [°] for adducts **7-12** [values in parentheses are for independent molecules].

Compound	**7**	**8**	**9**	**10**	**11**	**12**
Peri moieties	Br TePhI_2	Br_2TePh SPh	Br_2TePh SePh	I_2TePh SPh	I_2TePh SePh	$(BrTePh)_2O$
Peri-region distances and sub-van der Waals contacts						
E(1)···X/E	3.2050(11)	3.218(3)	3.2729(8)	3.141(4)	3.2677(18) [3.2862(18)]	3.335(1) [3.385(1)]
Σr_{vdW} - E···X/E; % ΣrvdW[a]	0.705; 82	0.642; 83	0.6871; 83	0.719; 81	0.6923; 83□[0.6738; 83]	0.785; 81 [0.735; 82]
E(1)-C(1)	2.135(5)	2.161(14)	2.148(7)	2.112(12)	2.117(10) [2.132(12)]	2.137(4) [2.131(5)]
X/E-C(9)	1.900(6)	1.821(15)	1.940(8)	1.800(14)	1.912(11) [1.937(11)]	2.135(4) [2.146(5)]
Acenaphthene bond lengths						
C(1)-C(2)	1.389(9)	1.364(19)	1.392(10)	1.358(16)	1.411(17) [1.363(16)]	1.380(7) [1.383(7)]
C(2)-C(3)	1.424(8)	1.42(3)	1.412(12)	1.379(18)	1.400(16) [1.451(16)]	1.407(6) [1.407(6)]
C(3)-C(4)	1.365(9)	1.402(18)	1.380(9)	1.351(17)	1.380(14) [1.356(19)]	1.362(7) [1.359(7)]
C(4)-C(5)	1.409(9)	1.369(19)	1.414(10)	1.414(17)	1.419(16) [1.413(17)]	1.406(7) [1.411(7)]
C(5)-C(10)	1.431(8)	1.43(3)	1.420(11)	1.380(18)	1.372(14) [1.429(16)]	1.420(6) [1.420(6)]
C(5)-C(6)	1.410(8)	1.382(17)	1.397(9)	1.422(19)	1.408(15) [1.390(17)]	1.416(6) [1.429(6)]
C(6)-C(7)	1.367(10)	1.409(18)	1.386(10)	1.347(19)	1.382(17) [1.390(19)]	1.355(7) [1.361(7)]
C(7)-C(8)	1.403(9)	1.41(3)	1.401(12)	1.42(2)	1.425(17) [1.414(17)]	1.415(6) [1.409(7)]
C(8)-C(9)	1.389(9)	1.389(18)	1.393(9)	1.380(19)	1.387(16) [1.363(17)]	1.379(6) [1.382(6)]
C(9)-C(10)	1.412(9)	1.382(17)	1.425(9)	1.446(16)	1.429(16) [1.438(16)]	1.434(6) [1.451(7)]
C(10)-C(1)	1.436(8)	1.438(16)	1.423(8)	1.465(16)	1.439(15) [1.424(17)]	1.444(6) [1.427(6)]
C(4)-C(11)	1.528(8)	1.54(3)	1.508(12)	1.536(19)	1.486(15) [1.532(18)]	1.516(6) [1.520(7)]
C(11)-C(12)	1.537(10)	1.532(17)	1.544(10)	1.529(19)	1.579(17) [1.54(2)]	1.528(7) [1.556(7)]
C(12)-C(6)	1.510(9)	1.49(2)	1.521(11)	1.53(2)	1.524(16) [1.509(18)]	1.518(6) [1.512(7)]
Peri-region bond angles						
E(1)-C(1)-C(10)	123.2(4)	121.8(10)	123.6(5)	122.8(8)	124.3(9) [122.7(9)]	124.0(3) [123.2(4)]
C(1)-C(10)-C(9)	131.8(5)	132.2(14)	131.1(7)	129.0(11)	128.7(10) [131.4(11)]	132.1(4) [132.3(4)]
X/E-C(9)-C(10)	121.8(4)	121.7(10)	122.6(5)	122.7(10)	122.3(8) [121.5(9)]	122.9(3) [124.6(3)]

Σ of bay angles	376.8(11)	375.7(27)	377.3(14)	374.5(23)	375.3(19) [375.6(22)]	379.0(8) [380.1(9)]
Splay angle^{b}	16.8	15.7	17.3	□4.5	15.3 [15.6]	19.0 [20.1]
C(4)-C(5)-C(6)	111.7(5)	113.1(14)	111.2(7)	112.3(11)	110.0(9) [112.1(11)]	111.1(4) [111.0(4)]
Out-of-plane displacement						
E(1)	-0.055(1)	0.493(1)	-0.447(1)	0.122(1)	-0.463(1) [-0.582(1)]	0.045(1) [0.099(1)]
X/E(1)	0.154(1)	-0.257(1)	0.217(1)	0.162(1)	0.487(1) [0.402(1)]	-0.139(1) [0.115(1)]
Central acenaphthene ring torsion angles						
C:(6)-(5)-(10)-(1)	179.52(1)	176.92(1)	-175.53(1)	-179.00(1)	-175.72(1) [-176.60(1)]	179.78(1) [179.01(1)]
C:(4)-(5)-(10)-(9)	-177.77(1)	175.99(1)	-177.49(1)	178.10(1)	175.82(1) [-172.96(1)]	176.60(1) [178.03(1)]

[a] van der Waals radii used for calculations: r_{vdW}(S) 1.80Å, r_{vdW}(Se) 1.90Å, r_{vdW}(Te) 2.06Å;[16] [b] Splay angle: Σ of the three bay region angles – 360.

Table S3 Non-bonded (hydrogen bond) intramolecular CH···π interactions [Å] and angles [°] for **4**-**11**.

	D-H···A	**H···A**	**D···A**	**D-H···A**
4 intra	C(14)-H(14)···Cg(20-25)	2.487(1)	3.432(1)	172.27(1)
4 inter	C(11)-H(11A)···Cg(1-5,10)	2.888(1)	3.641(1)	133.55(1)
4 inter	C(12)-H(12B)···C□(13-18)	2.984(1)	3.622(1)	123.19(1)
4 inter	C(16)-H(16)···Cg(13-18)	2.998(1)	3.886(1)	156.19(1)
5 intra	C(18)-H(18)···Cg(19-24)	2.510(1)	3.439(1)	177.69(1)
5 inter	C(11)-H(11B)···Cg(1-5,10)	2.901(1)	3.638(1)	139.59(1)
5 inter	C(16)-H(16)···Cg(13-18)	2.982(1)	3.839(1)	154.09(1)
6 inter	C(17)-H(17)···Cg(1-10)	2.755(1)	3.446(1)	130.27(1)
7 inter	C(11)-H(11B)···Cg(5-10)	2.798(1)	3.606(1)	139.07(1)
7 inter	C(12)-H(12A)···Cg(1-5,10)	2.689(1)	3.532(1)	143.55(1)
8 inter	C(17)-H(17)···Cg(1-5,10)	2.735(1)	3.619(1)	155.04(1)
9 inter	C(15)-H(15)···Cg(1-5,10)	2.749(1)	3.594(1)	148.42(1)
10 inter	C(15)-H(15)···Cg(1-5,10)	2.700(1)	3.598(1)	158.19(1)
10 inter	C(20)-H(20)···Cg(13-18)	2.879(1)	3.684(1)	143.23(1)
10 inter	C(22)-H(22)···Cg(5-10)	2.958(1)	3.764(1)	143.41(1)
11 inter	C(15)-H(15)···Cg(5-10)	2.713(1)	3.391(1)	128.96(1)

[a] Cg(20–25) is the centroid of atoms C(20)–C(25).

4. References

1 F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin and J. D. Woollins, *Inorg. Chem.*, 2010, **49**, 7577.

2 A. D. Becke, J. *Chem. Phys***.,** 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

3 R. C. Binning and L. A. Curtiss, *J. Comput. Chem.*, 1990*,* **11**, 1206.

4 P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762; A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431.

5 S. Huzinaga, J. Anzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, in: *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, 1984.

6

7 A. E. Reed, F. Curtiss and L. A. F. Weinhold, *Chem. Rev.,* 1988, **88**, 899.

8 As implemented in G03: V. Barone, M. Cossi and J. Tomasi, *J. Comput. Chem.*, 1998, **19**, 404; M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys*., 2002, **117**, 43; M. Cossi and O. Crescenzi, *J. Chem. Phys.*, 2003, **19**, 8863.

9 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

10 S. F. Boys and F. Bernardi, *Mol. Phys.,* 1970, **19**, 553.

11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.

12 A. L Fuller, L. A. S. Scott-Hayward, Y. Li, M. Bühl, A. M. Z. Slawin and J. D. Woollins*, J. Am. Chem. Soc.*, 2010, **132**, 5799.

13 CrystalClear 2.0: Rigaku Corporation, 2010. CrystalClear Software User's Guide, Molecular Structure Corporation, © 2000. J. W. P. Flugrath, *Acta Crystallogr., Sect. D,* 1999, **D55**, 1718.

14 CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2009). 9009 New Trails Dr., The Woodlands, TX 77381, USA.

15 SHELX97: G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 2008, **64**, 112.

16 A. Bondi, *J. Phys. Chem*., 1964, **68**, 441.