Supporting Information

Experimental

General

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring, unless otherwise indicated. The term "concentrated *in vacuo*" refers to removal of solvents by rotary evaporation. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl immediately prior to use. Methanol (Fischer), $Pd(PPh_3)_4$ (Strem), 2.0 M butylmagnesium chloride in THF (Aldrich), $^{13}C_2$-acetylene (Cambridge Isotope Laboratories), 1,3-cyclohexadiene (Aldrich), and $ZnCl_2$ (Strem) were used without further purification. Column chromatography was carried out with ICN SiliTech 32-63 D 60 Å silica gel.

The ^{1}H NMR data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (TMS), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). The ^{13}C spectra were determined with complete proton decoupling. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrophotometer.

Bis(2-trimethylsilylethynylphenyl)-$^{13}C_2$-ethyne (8). A Schlenk flask was connected by tubing (containing a magnetic stir bar) to a sealed flask containing 34 mL (1.52 mmol) of $^{13}C_2$-acetylene. The Schlenk flask was charged with 15 mL of THF, which was degassed with nitrogen, chilled to –78 °C, and 1.52 mL (3.04 mmol) of 2.0 M butylmagnesium chloride in THF were added. It was then placed in liquid nitrogen, evacuated, and the exit port closed. The magnetic stir bar in the hose was used to break the seal on the flask containing the acetylene. The Schlenk flask was left open to the acetylene for 10 min, after which it was sealed and left at –78 °C for 25 min. The solution was then allowed to warm to room temperature for 70 min. The flask was placed under nitrogen, and 414 mg (3.04 mmol) of $ZnCl_2$ were added under strong nitrogen purge. After the cloudy reaction mixture had been stirred for 30 min, 0.980g

(3.26 mmol) of 1-iodo-2-trimethylsilylethynylbenzene[1] in 5 mL of THF was injected by syringe. $Pd(PPh_3)_4$ (200 mg, 0.17 mmol) was added under strong nitrogen purge and the vessel fitted with a condenser. After heating to reflux for 3 d, 100 mL of saturated NH_4Cl solution were added and the mixture extracted with ether (2 x 150 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed with 99:1 petroleum ether/diethyl ether. Crystallization from ethanol yielded 269 mg (48%) of **8** as a yellow solid.

Data for **8**: IR (KBr) 2959, 2897, 2158, 1486, 1445, 1245, 875, 845, 760 cm^{-1}. MS (70 eV) (*m/z*): 372 (M^+, 3), 358 (11), 357 (30), 342 (35), 341 (100), 300 (10), 285 (20). ^1H NMR (500 MHz, $CDCl_3$): δ 7.58-7.52 (m, 2), 7.52-7.47 (m, 2), 7.33-7.23 (m, 4), 0.26 (s, 18). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.2 (t, J = 2.2), 131.9 (t, J = 2.0),128.1 (t, J = 2.7), 128.0, 126.1 (t, J = 53.4), 125.6 (t, J = 1.7), 103.4, 98.7, 92.0 (^{13}C-enriched), 0.0.

Bis(2-ethynylphenyl)-$^{13}C_2$-ethyne. A round-bottomed flask was charged with 955 mg (2.57 mmol) of bis(2-trimethylsilylethynylphenyl)-$^{13}C_2$-ethyne (**8**), 724 mg (18.1 mmol) of sodium hydroxide, and 40 mL of methanol. After 18 h, 100 mL of 0.5 M HCl were added and the solution extracted with ether (2 x 100 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed with 9:1 hexanes/diethyl ether to afford 557 mg (95%) of bis(2-ethynylphenyl)-$^{13}C_2$-ethyne as a white solid.

Data for bis(2-ethynylphenyl)-$^{13}C_2$-ethyne: IR (KBr) 3282, 3059, 1484, 1445, 761, 666, 636 cm^{-1}. MS (70 eV) (*m/z*): 229 (19), 228 (M^+, 100), 227 (34), 226 (55), 225 (14), 202 (10), 114 (10), 113 (17). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60-7.55 (m, 2), 7.55-7.50 (m, 2), 7.35-7.25 (m, 4), 3.33 (s, 2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.6 (t, J = 2.2), 132.3 (t, J = 2.0), 128.5 (t, J = 2.7), 128.2, 126.2 (t, J = 53.3), 124.5 (t, J = 1.6), 91.7 (^{13}C-enriched), 82.1 (t, J = 1.5), 81.3.

[1] Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969.

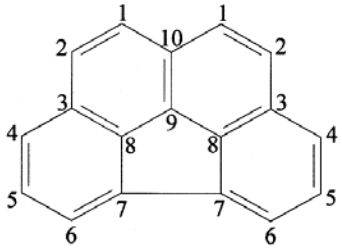
$^{13}C_2$-Angular [3]Phenylene (2a). A 100 mL Schlenk flask was charged with 99 mg (0.43 mmol) of bis(2-ethynylphenyl)-$^{13}C_2$-ethyne and 20 mL of THF and chilled to –25 °C. Similarly, a 50 mL round-bottomed flask containing 86 mg (0.48 mmol) of cyclopentadienylbis(ethene)cobalt[2] and 10 mL of THF was cooled to –78 °C. This solution was added by cannula to the Schlenk flask and left to stir at –25 °C. After 19 h, 0.80 mL of 1,3-cyclohexadiene was injected by syringe, the flask sealed, and the solution heated to 100 °C for 45 min. The mixture was concentrated *in vacuo* and the residue chromatographed with hexanes to afford 30 mg (30%) of **2a** as a yellow solid.

Data for **2**: IR (KBr) 3051, 1415, 1376, 1157, 933, 831, 744 cm^{-1}. MS (70 eV) (*m/z*): 229 (19), 228 (M^+, 100), 227 (31), 226 (37), 225 (9). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.03-6.93 (m, 6), 6.93-6.87 (m, 2), 6.18 (dd, 2, *J* = 4.1, 3.4). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 151.0 (t, *J* = 2.4), 149.6 (dd, *J* = 18.8, 17.6), 149.5 (dd, *J* = 25.0, 24.4), 136.1 (^{13}C-enriched), 129.4, 128.8 (t, *J* = 2.2), 119.8, 118.7 (t, *J* = 4.5), 114.6 (t, *J* = 1.9).

(2) Jonas, K.; Deffense, E. Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716.

^{13}C NMR Assignments

Benzo[*ghi*]fluoranthene (3)



The ^{13}C NMR spectrum of **3**-$^{13}C_2$ isolated from the FVP of **2a** exhibits two major labeling patterns: a doublet at δ 137.3 (J = 53.1 Hz) correlated to a doublet at δ 133.2 (J = 53.1 Hz), and a smaller doublet at δ 133.0 (J = 56.0 Hz) correlated to a doublet at δ 126.7 (J = 55.9 Hz).

Although **3** contains 18 carbons, because of the symmetry of the molecule there are only 10 signals in its ^{13}C NMR spectrum. Five of these (δ 128.3, 126.6, 126.3, 125.0, and 123.4) are due to tertiary carbon atoms (determined by HMQC) and five (δ 137.3, 133.2, 133.0, 127.6, and 126.7) are assignable to quaternary ones.

The doublet at δ 8.15 (J = 7.0 Hz) in the ^{1}H NMR spectrum is assigned to H-6.[3] From the HMQC it can be determined that the ^{13}C NMR signal at δ 123.4 is from C-6. The doublet of doublets at δ 7.71 (J = 8.0, 7.0 Hz) arises clearly from H-5, and by HMQC the peak at δ 128.3 is due to C-5. This allows the doublet at δ 7.96 (J = 8.0 Hz) to be assigned to H-4 (the ^{13}C signal at δ 126.3 is caused by C-4). Finally, the doublets at δ 8.00 (J = 8.7 Hz, HMQC correlated carbon signal at δ 126.6) and δ 7.95 (J = 8.7 Hz, correlated carbon signal at δ 125.0) have their origin in H-1 and H-2.

Further information was obtained from a long-range HMQC spectrum optimized to look for couplings of 7 Hz. H-5 correlates with carbon signals at δ 128.3 (C-5), 127.6, and 137.3. As this type of experiment most often shows three-bond or two-bond

(3) Brooks, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 5444.

couplings,[4] it is highly likely that the quaternary carbon signals at δ 127.6 and 137.3 arise from C-3 and C-7.

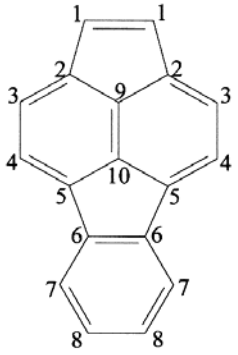
H-6 correlates with carbon signals at δ 128.3 (C-5), 126.3 (C-4), 123.4 (C-6), 137.3 and 133.2. This leads to the conclusion that the signal at δ 137.3 belongs to C-7, because the two-bond coupling between H-6 and C-7 is much more likely to be observed than a four-bond coupling between H-6 and C-3. This allows the signal at δ 127.6 to be assigned to C-3. The observed correlation between H-6 and the signal at δ 133.2 suggests that this signal is due to C-8, as the three-bond coupling to C-8 is more likely to be observed than a long range coupling to C-9 or C-10. The only remaining unassigned signals (δ 133.0 and 126.7) are therefore due to C-9 and C-10.

C-8 shows a correlation with the proton signal at δ 8.00. Since the three-bond coupling between C-8 and H-2 is more likely to be observed than the four-bond coupling between C-8 and H-1, this leads to the conclusion that the signal at δ 125.0 is from C-1 and the signal at δ 126.6 is due to C-2.

To summarize the ^{13}C NMR assignments: δ 125.0 (C-1), 126.6 (C-2), 127.6 (C-3), 126.3 (C-4), 128.3 (C-5), 123.4 (C-6), 137.3 (C-7), 133.2 (C-8), 133.0 and 126.7 (C-9 and C-10). The larger pair of doublets observed in the ^{13}C NMR spectrum of **3**-$^{13}C_2$ (J = 53.1 Hz) can be assigned to C-7 and C-8, while the smaller pair of doublets (J = 56.0 Hz) is due to C-9 and C-10.

(4) Claridge, T. D. W. *High-Resolution NMR Techniques in Organic Chemistry*; Pergamon: New York, 1999; Chapter 6, pp. 221-257.

Acefluoranthylene (4)



The ^{13}C NMR spectrum of **4**-$^{13}C_2$ isolated from the FVP of **2a** exhibits two major labeling patterns: a doublet at δ 138.8 (J = 49.6 Hz) correlated to a doublet at δ 132.9 (J = 49.6 Hz), and a smaller doublet also at δ 138.8 (J = 68.5 Hz) correlated to a doublet at δ 121.1 (J = 68.5 Hz).

Although **4** contains 18 carbons, because of the symmetry of the molecule there are only 10 signals in its ^{13}C NMR spectrum. Five of these (δ 131.6, 128.4, 125.7, 122.9, and 121.1) are due to tertiary carbon atoms (determined by HMQC) and five (δ 142.8, 140.6, 138.8, 132.9, and 130.4) are assignable to quaternary ones.

The singlet at δ 6.52 in the ^{1}H NMR spectrum arises clearly from H-1. From the HMQC it can be determined that the ^{13}C NMR signal at δ 131.6 is caused by C-1. The doublets at δ 7.19 and 7.13 arise from H-4 and H-3. A NOESY spectrum of **4** reveals a cross peak between the singlet at δ 6.52 and the doublet at δ 7.13. This shows that the proton signal at 7.13 ppm is from to H-3, and by HMQC the peak at δ 125.7 is due to C-3. By elimination, the doublet at δ 7.19 is caused by H-4 (δ 121.1 is due to C-4). The NOESY spectrum also shows a cross peak between H-4 and the multiplet at δ 7.36, consistent with this signal originating from H-7 (the signal at δ 122.9 belongs to C-7), allowing the multiplet at δ 7.03 to be assigned to H-8 (and δ 128.4 to C-8).

Further information can be obtained from an HMBC spectrum. H-1 correlates with carbon signals at δ 131.6 (C-1), 130.4, and 140.6. As HMBCs most often show three-bond or two-bond couplings,[4] it is highly likely that the quaternary carbon signals at δ 130.4 and 140.6 arise from C-2 and C-9.

H-3 correlates with carbon signals at δ 121.4 (C-4), 131.6 (C-1), 130.4, and 138.8. This leads to the conclusion that the signal at δ 138.8 belongs to C-5, as it is not from C-2 or C-9 (because they cause the signals at δ 130.4 or 140.6), and the three-bond coupling between H-3 and C-5 is much more likely to be observed in an HMBC than a four-bond coupling between H-3 and C-6 or C-10.

H-4 correlates with carbons signals at δ 125.7 (C-3), 132.9, 140.6, and 142.8. From this and preceding data the conclusion can be drawn that the signal at δ 140.6 is due to C-2, as the correlation between H-4 and C-2 (a three-bond coupling) is much more likely to be observed in a HMBC than the correlation between H-4 and C-9 (a four-bond coupling). This means that the signal at δ 130.4 arises from C-9.

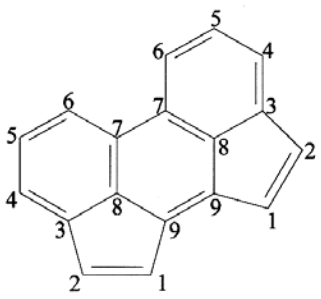
H-8 only correlates with signals at δ 122.9 (C-7) and 142.8. This strongly suggests that the signal at δ 142.8 is due to C-6 (a three-bond coupling to H-8).

H-7 correlates with signals at δ 128.4 (C-8), 138.8, and 142.8 (C-6). As the three-bond coupling between H-7 and C-5 is more likely to be observed than the four-bond coupling between H-7 and C-10, the signal at δ 138.8 can be assigned to C-5. By elimination, the signal at δ 132.9 is due to C-10.

These assignments are also consistent with the lesser intensity of the peaks at δ 130.4 and 132.9. Assigning these peaks to C-9 and C-10 is thus reasonable, as these carbons are quaternary and their relative abundance is half that of the other carbons.

To summarize the ^{13}C NMR assignments: δ 131.6 (C-1), 140.6 (C-2), 125.7 (C-3), 121.1 (C-4), 138.8 (C-5), 142.8 (C-6), 122.9 (C-7), 128.4 (C-8), 130.4 (C-9), 132.9 (C-10). The larger pair of doublets observed in the ^{13}C NMR spectrum of **4**-$^{13}C_2$ (J = 49.6 Hz) can be assigned to C-5 and C-10, while the smaller pair of doublets (J = 68.5 Hz) is due to C-5 and C-4.

Cyclopent[*hi*]acephenanthrylene (5)



The ^{13}C NMR spectrum of **5**-$^{13}C_2$ isolated from the FVP of **2a** exhibits two major labeling patterns: a singlet at δ 136.2, and a less intense doublet at δ 130.8 (J = 61.0 Hz) correlated to a doublet at δ 126.2 (J = 61.0 Hz).

The ^{1}H and ^{13}C NMR spectra of **5** have been previously assigned,[5] but since literature ^{13}C NMR assignments of PAH's have on occasion proven to be incorrect (see, for instance, the section on cyclopenta[*cd*]pyrene), the assignment was confirmed.

Although **5** has 18 carbons, because of the symmetry of the molecule there are only 9 signals in its ^{13}C NMR spectrum. Five of these (δ 135.5, 128.0, 126.0, 123.0, and 122.2) are due to tertiary carbon atoms (determined by HMQC) and four (δ 139.6, 136.2, 130.8, and 126.2) are assignable to quaternary ones.

The doublet of doublets at δ 8.38 is known to be due to H-6.[6] From the HMQC it can be determined that the ^{13}C NMR signal at δ 122.2 ppm is from C-6. The doublet at δ 7.28 is caused by H-1 (δ 126.0 is from C-1) and the doublet at δ 7.40 arises from H-2 (δ 135.5 is from C-2). The doublet of doublets at δ 7.73 is due to H-4 (δ 123.0 is from C-4) and the doublet of doublets at δ 7.69 has its origin in H-5 (δ 128.0 is from C-5).

Further information can be obtained from an HMBC spectrum. H-6 correlates with carbon signals at δ 123.0 (C-4), 126.2, and 130.8. As HMBCs most often show three-bond or two-bond couplings,[4] it is highly likely that the quaternary carbon signals at δ 126.2 and 130.8 arise from C-7 and C-8.

H-1 correlates with carbon signals at δ 135.5 (C-2), 130.8, 136.2 and 139.6. This leads to the conclusion that the signal at δ 130.8 belongs to C-8, as this is the carbon most

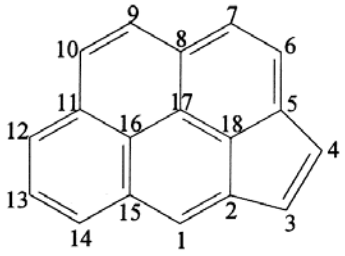
[5] Mulder, P. P. J.; Boere, B. B.; Cornelisse, J.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 255.

likely to correlate with both H-1 and H-6 (a three-bond coupling in each case). C-8 also shows the expected correlation with H-4 (another three-bond coupling). The signals at δ 136.2 and 139.6 are therefore from C-9 and C-3. H-5 correlates with the signal at δ 139.6, but not the signal at δ 136.2, leading to the conclusion that the peak at δ 139.6 is due to C-3 and that at δ 136.2 to C-9.

To summarize the ^{13}C NMR assignments: δ 126.0 (C-1), 135.5 (C-2), 139.6 (C-3), 123.0 (C-4), 128.0 (C-5), 122.2 (C-6), 126.2 (C-7), 130.8 (C-8), 136.2 (C-9). These assignments are identical to those previously published.[5] The large singlet observed in the ^{13}C NMR spectrum of **5**-$^{13}C_2$ can be assigned to C-9, while the large pair of doublets is due to C-7 and C-8.

[6] Banciu, M. D.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Jurss, C.; Mavropoulos, I.; Stanescu, M.; Wiersum, U. E. *Aust J. Chem*., **1996**, *49*, 965.

Cyclopenta[*cd*]pyrene (6)



The ^{13}C NMR spectrum of **6**-$^{13}C_2$ isolated from the FVP of **2a** exhibits two major labeling patterns: a doublet at δ 131.7 (J = 56.7 Hz) correlated to a doublet at δ 122.0 (J = 56.7 Hz), and a less intense doublet at δ 130.6 (J = 52.9 Hz) correlated to a doublet at δ 120.4 (J = 52.7 Hz).

Using published ^{1}H and ^{13}C assignments,[7] the signals can be assigned as follows: the signal at δ 131.7 is from C-15, δ 122.0 from C-17, δ 130.6 from C-5, and δ 120.4 from C-16. It is clear from the data above that these assignments cannot be correct. The 57 Hz coupling constant is too large for a two-bond aromatic C-C coupling, and the 53 Hz coupling constant is far too large for a three-bond aromatic C-C coupling. It was thus necessary to subject this compound to renewed analysis, now aided by the presence of the labels.

Cyclopenta[*cd*]pyrene has 18 carbons. Ten of these (δ 133.2, 130.3, 128.3, 127.5, 126.70, 126.68, 126.4, 126.2, 124.1, and 122.4) are due to tertiary carbon atoms (determined by HMQC) and eight (δ 138.8, 135.3, 131.7, 130.6, 130.0, 127.1, 122.0 and 120.4) to quaternary ones, including the four signals of primary interest.

The singlet at δ 8.39 in the ^{1}H NMR spectrum arises clearly from H-1. From the HMQC it can be determined that the ^{13}C NMR signal at 126.2 ppm is from C-1. The doublet at δ 7.25 (J = 5.1 Hz, HMQC correlated carbon signal at δ 127.5) has been shown by selective deuterium labeling to be due to H-3,[8] which means that the doublet at δ 7.43 is caused by H-4 (J = 5.1 Hz , the signal at δ 133.2 is from C-4). A NOESY spectrum of **6** reveals a cross peak between the singlet at δ 8.39 and the signal at δ 8.43. This shows that the proton at 8.43 ppm is H-14 (δ 130.3 is due to C-14).

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[7] Jans, A. W. H.; Tintel, C.; Cornelisse, J.; Lugtenburg, J. *Magn. Reson. Chem.* **1986**, *24*, 101.
[8] Sahali, Y.; Kwon, H.; Skipper, P.; Tannenbaum, S. R. *Chem. Res. Toxicol*. **1992**, *5*, 157.

Further information can be obtained from a long range HMQC optimized to look for couplings of 10 Hz. Both H-3 and H-4 clearly correlate with five carbons. Two of these (with signals at δ 127.5 and 133.2) are tertiary (C-3 and C-4) and three are quaternary (with signals at δ 127.1, 135.3, and 138.8). As three-bond and two-bond couplings are the most likely to be observed under these conditions,[4] it is highly probable that the three correlations to quaternary carbons that are observed are between H-3 and H-4 and C-2, C-5, and C-18. This leaves C-8, C-11, C-15, C-16, and C-17 as possible locations for the labels with signals at δ 131.7, 122.0, 130.6, and 120.4.

H-1 correlates with one tertiary carbon (δ 130.3, C-14) and three quaternary carbons with signals at δ 122.0, 127.1 (arising potentially from either C-2, C-5, or C-18, C-5 being unlikely, as it would require a four-bond coupling), and 131.7. It is highly likely that the labeled signals at δ 122.0 and 131.7 are from C-15 and C-16, as the long range HMQC can be expected to show primarily three-bond and two-bond couplings, and C-2 and C-18 are already assigned. This leaves C-8, C-11, and C-17 as possible locations for the labels observed at δ 120.4 and 130.6. Because of the large coupling constants between the labeled signals at δ 120.4 and 130.6 (J = 53 Hz), it is clear that the two labeled carbons must be adjacent and therefore be C-8 and C-17. By elimination, this also means that the signal at δ 130.0 is due to C-11.

There is further information that can be obtained from the spectra. The signal at δ 122.0 correlates with four protons, meaning that it is almost definitely C-16, because C-15 could only correlate with at most three protons by three-bond or two-bond couplings (H-1, H-13, and H-14) while C-16 can correlate with four (H-1, H-14, H-12, and H-10). This leaves the signal at δ 131.7 to be caused by C-15.

The signal at δ 127.1 (already determined to be either C-2 or C-18) correlates with four protons, indicating its origin as C-18, which can correlate by three-bond or two-bond couplings with H-1, H-3, H-4, and H-6, instead of C-2, which can only correlate with three protons (H-1, H-3, and H-4). This means that the peaks at δ 135.3 and 138.8 are due to C-2 and C-5. The signal at δ 135.3 correlates with H-3, H-4, and a proton which is not H-1 (either H-6 or H-7). Therefore, the signal at δ 135.3 is from C-5, leaving the peak at δ 138.8 to be due to C-2.

To summarize the ^{13}C NMR assignments: δ 126.2 (C-1), 138.8 (C-2), 127.5 (C-3), δ 133.2 (C-4), δ 135.3 (C-5), 120.4 and 130.6 (C-8 and C-17), 130.0 (C-11), 130.3 (C-14), 131.7 (C-15), 122.0 (C-16), 127.1 (C-18). The larger pair of doublets observed in the ^{13}C NMR spectrum of **6**-$^{13}C_2$ (J = 52.8 Hz) can be assigned to C-8 and C-17, while the smaller pair of doublets (J = 56.7 Hz) is due to C-15 and C-16.