# Supplementary data

# Synthesis, Single Crystal X-Ray Hirshfeld and DFT studies of 1,8-Dichloro-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid

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*1.1. X-Ray single crystal measurements of* **5**

Intensity data have been collected at room-temperature on a Bruker SMART APEX II D8 and CuK$\alpha$-radiation ($\lambda$ = 1.54178 Å), at University of Karachi, Pakistan. The crystal size was 0.40 × 0.23 × 0.11 $mm^3$.For compound **5**, the frames were integrated with the Bruker SAINT software package using a narrow frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 17655 reflections to a maximum θ angle of 68.50° (0.83 Å resolution), of which 2534 were independent (average redundancy 6.967, completeness = 98.2%, $R_{int}$ = 3.03%, $R_{sig}$ = 1.82%) and 2503 (98.78%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.735(2) Å, b = 8.0225(12) Å, c = 12.0928(16) Å, $\alpha$ = 88.430(14)°, $\beta$ = 82.549(13)°, $\gamma$ = 70.46(2)°, volume = 701.1(3) $Å^3$, (Table S1) are based upon the refinement of the XYZ-centroids of 9910 reflections above 20 $\sigma$(I) with 7.375° < 2θ < 136.5°. Data were corrected for absorption effects using the (SADABS) Multi-Scan method. The ratio of minimum to maximum apparent transmission was 0.856. The calculated minimum and maximum transmission coefficients (depend on size of crystal) are 0.6445 and 0.7531. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{17}H_{12}Cl_2O_2$. The final anisotropic full-matrix least squares refinement on $F^2$ with 193 variables converged at R1 = 3.16%, for the observed data and wR2 = 8.40% for all data. The goodness of fit was 1.081. The H atoms bonded to C were positioned with idealized geometry using a riding model with C—H = 0.93 Å (aromatic), 0.97 Å (CH2) and 0.98 Å (CH). The hydroxyl H atom was refined with the O—H distance restrained to 0.82 Å. All H atoms were assigned isotropic displacement parameters $U_{iso}$(H) = 1.2Ueq of the parent atoms.

**Table S1.** The calculated geometric parameters of **5**[a].

| Parameter | Calc | Exp | Parameter | Calc | Exp |
|---|---|---|---|---|---|
| R(1-26) | 1.763 | 1.747 | A(6-7-8) | 112.3 | 112.1 |
| R(2-10) | 1.763 | 1.739 | A(6-7-9) | 107.6 | 107.0 |
| R(3-32) | 1.210 | 1.223 | A(6-7-27) | 106.6 | 106.4 |
| R(4-32) | 1.358 | 1.321 | A(6-26-24) | 120.9 | 121.0 |
| R(5-6) | 1.407 | 1.403 | A(8-7-9) | 112.4 | 112.0 |
| R(5-18) | 1.518 | 1.516 | A(8-7-27) | 110.9 | 112.0 |
| R(5-20) | 1.391 | 1.385 | A(9-7-27) | 106.7 | 106.9 |
| R(6-7) | 1.518 | 1.515 | A(7-9-10) | 128.2 | 128.5 |
| R(6-26) | 1.392 | 1.384 | A(7-9-17) | 113.2 | 113.4 |
| R(7-9) | 1.519 | 1.517 | A(7-27-28) | 109.2 | 109.8 |
| R(7-27) | 1.565 | 1.559 | A(7-27-29) | 109.7 | 109.8 |
| R(9-10) | 1.392 | 1.384 | A(7-27-30) | 109.7 | 109.4 |
| R(9-17) | 1.407 | 1.400 | A(10-9-17) | 118.6 | 118.2 |
| R(10-11) | 1.399 | 1.394 | A(9-10-11) | 120.9 | 121.3 |
| R(11-13) | 1.393 | 1.384 | A(9-17-15) | 121.2 | 121.4 |
| R(13-15) | 1.398 | 1.393 | A(9-17-18) | 112.9 | 113.1 |
| R(15-17) | 1.390 | 1.390 | A(10-11-12) | 119.6 | 120.3 |
| R(17-18) | 1.518 | 1.513 | A(10-11-13) | 119.6 | 119.5 |
| R(18-30) | 1.579 | 1.564 | A(12-11-13) | 120.9 | 120.2 |
| R(20-22) | 1.398 | 1.397 | A(11-13-14) | 119.4 | 119.7 |
| R(22-24) | 1.393 | 1.386 | A(11-13-15) | 120.5 | 120.5 |
| R(24-26) | 1.398 | 1.397 | A(14-13-15) | 120.1 | 119.7 |
| R(27-30) | 1.551 | 1.552 | A(13-15-16) | 120.5 | 120.5 |
| R(30-32) | 1.521 | 1.521 | A(13-15-17) | 119.2 | 119.0 |
| A(1-26-6) | 120.7 | 120.2 | A(16-15-17) | 120.3 | 120.5 |
| A(1-26-24) | 118.4 | 118.7 | A(15-17-18) | 125.9 | 125.5 |
| A(2-10-9) | 120.6 | 120.5 | A(17-18-19) | 112.4 | 112.0 |
| A(2-10-11) | 118.4 | 118.1 | A(17-18-30) | 106.1 | 107.3 |
| A(3-32-4) | 122.1 | 123.4 | A(19-18-30) | 110.6 | 112.0 |
| A(3-32-30) | 126.7 | 123.3 | A(18-30-27) | 109.1 | 109.7 |
| A(32-4-33) | 106.0 | 112.3 | A(18-30-31) | 106.9 | 107.8 |
| A(4-32-30) | 111.1 | 113.3 | A(18-30-32) | 111.1 | 110.2 |
| A(6-5-18) | 112.8 | 112.9 | A(21-20-22) | 120.5 | 120.5 |
| A(6-5-20) | 121.2 | 121.4 | A(20-22-23) | 120.1 | 119.7 |
| A(5-6-7) | 113.3 | 113.5 | A(20-22-24) | 120.5 | 120.7 |
| A(5-6-26) | 118.6 | 118.5 | A(23-22-24) | 119.4 | 119.7 |
| A(18-5-20) | 126.0 | 125.7 | A(22-24-25) | 120.8 | 120.3 |
| A(5-18-17) | 108.1 | 107.8 | A(22-24-26) | 119.6 | 119.4 |
| A(5-18-19) | 112.4 | 112.0 | A(25-24-26) | 119.5 | 120.3 |
| A(5-18-30) | 106.9 | 105.3 | A(28-27-29) | 108.0 | 108.2 |
| A(5-20-21) | 120.3 | 120.5 | A(28-27-30) | 110.6 | 109.8 |
| A(5-20-22) | 119.2 | 119.0 | A(29-27-30) | 109.7 | 109.8 |
| A(7-6-26) | 128.1 | 128.0 | A(27-30-31) | 111.0 | 107.8 |
| | | | A(27-30-32) | 112.6 | 113.4 |

| | | | |
|---|---|---|---|
| | A(31-30-32) | 106.1 | 107.8 |

[a]Atom numbering refer to **Figure 1**

**Table S2.** The calculated natural charges of **5**[a].

| Atom | Charge | Atom | Charge |
|---|---|---|---|
| Cl 1 | -0.0067 | C18 | -0.2669 |
| Cl 2 | -0.0073 | H19 | 0.2796 |
| O 3 | -0.5915 | C20 | -0.2290 |
| O 4 | -0.7223 | H21 | 0.2439 |
| C 5 | -0.0191 | C22 | -0.2222 |
| C 6 | -0.0368 | H23 | 0.2466 |
| C 7 | -0.2807 | C24 | -0.2462 |
| H 8 | 0.2928 | H25 | 0.2573 |
| C 9 | -0.0388 | C26 | -0.0214 |
| C10 | -0.0237 | C27 | -0.4537 |
| C11 | -0.2482 | H28 | 0.2564 |
| H12 | 0.2573 | H29 | 0.2757 |
| C13 | -0.2233 | C30 | -0.3549 |
| H14 | 0.2469 | H31 | 0.2842 |
| C15 | -0.2298 | C32 | 0.8436 |
| H16 | 0.2437 | H33 | 0.5059 |
| C17 | -0.0112 | | |

[a]Atom numbering refer to **Figure 1**

**Table S3.** Calculated and experimental $^{1}H$ and $^{13}C$ NMR chemical shifts for **5**[a].

| Atom | $CS_{calc}$ | $CS_{exp}$ | Atom | $CS_{calc}$ | $CS_{exp}$ |
|---|---|---|---|---|---|
| C 5 | 131.379 | 143.04 | H 8 | 5.332 | 5.16 |
| C 6 | 129.248 | 139.73 | H12 | 7.483 | 7.225 |
| C 7 | 33.450 | 46.67 | H14 | 7.550 | 7.225 |
| C 9 | 129.705 | 139.84 | H16 | 7.661 | 7.225 |
| C10 | 126.463 | 128.24 | H19 | 4.937 | 4.81 |
| C11 | 114.759 | 126.14 | H21 | 7.549 | 7.225 |
| C13 | 115.178 | 127.46 | H23 | 7.523 | 7.225 |
| C15 | 111.121 | 122.82 | H25 | 7.495 | 7.225 |
| C17 | 134.340 | 145.51 | H28 | 2.039 | 1.85 |
| C18 | 44.259 | 42.95 | H29 | 2.481 | 1.995 |
| C20 | 111.504 | 124.08 | H31 | 3.108 | 2.75 |
| C22 | 115.148 | 127.22 | H33 | 6.716 | - |
| C24 | 114.955 | 126.20 | | | |
| C26 | 126.411 | 127.81 | | | |
| C27 | 24.289 | 28.49 | | | |
| C30 | 38.774 | 36.48 | | | |
| C32 | 159.826 | 173.88 | | | |

[a]Atom numbering refer to **Figure 1**