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# Dissociative electron transfer in polychlorinated aromatics. Reduction potentials from convolution analysis and quantum chemical calculations

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## Supplementary Information

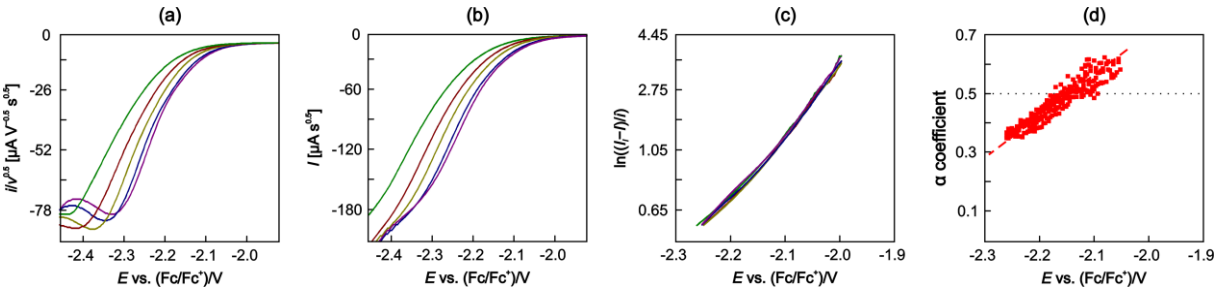


**Fig. S1.** Successive steps of transfer coefficient calculation, from voltammograms divided by the square root of scan rate (a), through semi-integrals (b) and $\ln((I_l-I(E))/i(E))$ vs. $E$ (c), to transfer coefficient, $\alpha$ vs. $E$ (d). Calculations were done for 3 mM pentachloroanisole at GCE in DMF/0.1 M $n$-$Bu_4NBF_4$ using scan rates, $v$ = 1, 2, 5, 10 and 20 V $s^{-1}$.

**Table S1.** Zero-point corrected gas-phase electron affinities (eV) computed at DFT:B3LYP-D2/6-311++G(2d) and CCSD(T)-F12/aug-cc-pVTZ levels (using Hartree-Fock or B3LYP reference determinants and the B3LYP/6-31+G(d) structures), and a Petersson's Complete Basis Set method, CBS-QB3 (ref. 29 in the main text).

| Reaction | DFT-D | HF-CC-F12a (F12b) | KS-CC-F12a (F12b) | CBS-QB3 | Exp |
|---|---|---|---|---|---|
| $C_6Cl_6 + e^- = C_6Cl_6^{\bullet-}$ | 1.35 | 0.82 (0.81) [a] | 0.90 (0.88) [b] | 0.90 | 0.92 ± 0.10 [c] |
| $Cl^\bullet + e^- = Cl^-$ | 3.68 [d] | 3.61 [d] (3.59 [d]) | | | 3.6131 [e] |

[a] $T_1^{HF}$ and $D_1^{HF}$ diagnostics for $C_6Cl_6^{\bullet-}$ are 0.017 and 0.108, respectively.
[b] $T_1^{KS}$ and $D_1^{KS}$ diagnostics for $C_6Cl_6^{\bullet-}$ are 0.014 and 0.077, respectively.
[c] W. B. Knighton, J. A. Bognar and E. P. Grimsrud, *J. Mass Spectrom.*, 1995, 30, 557–562.
[d] Includes spin-orbit correction for $Cl^\bullet$ (−36.5 meV).
[e] J. D. D. Martin and J. W. Hepburn, *J. Chem. Phys.*, 1998, 109, 8139–8142.

**Table S2.** Zero-point corrected C−Cl bond homolytic dissociation energies (kcal·$mol^{-1}$) computed at DFT:B3LYP-D2/6-311++G(2d,2p) and CCSD(T)-F12/aug-cc-pVTZ levels in the gas phase using the B3LYP/6-31+G(d,p) structures.

| Reaction | DFT-D | HF-CC-F12a (F12b) [a] |
|---|---|---|
| $C_6Cl_5OMe = C_6Cl_4OMe^\bullet + Cl^\bullet$ | 85.7 | 95.6 (95.3) |
| 2,4-D = [2,4-D – 2-Cl]$^\bullet$ + $Cl^\bullet$ | 90.1 | 97.0 (96.7) |
| 2,4,5-T = [2,4,5-T – 5-Cl]$^\bullet$ + $Cl^\bullet$ | 89.5 | 96.9 (96.6) |

[a] For chlorophenoxyacetic acids an extrapolation scheme was applied, see Computational Methods in the main text.

**Table S3.** $\Delta\Delta_{solv}G^0$ for $C_6Cl_6/C_6Cl_6^{\bullet-}$ redox couple calculated at B3LYP/6-31+G(d) (or BP86/TZVP in the case of COSMO-RS) level using gas-phase geometries optimised at the same level of theory.

| Solvent model | $\Delta\Delta_{solv}G^0$ (eV) [a] |
|---|---|
| IEFPCM-UFF | −1.57 |
| SMD | −1.52 |
| CPCM-UAKS | −1.52 |
| COSMO-RS | −1.61 |
| Exp [b] | −2.0 |

[a] $\Delta_{solv}G^0$(anion) – $\Delta_{solv}G^0$(neutral).
[b] Mean value of the experimental $\Delta\Delta_{solv}G^0$ for a couple of symmetrical polychlorinated benzenes from J.R. Wiley, *et al.*, *J. Electroanal. Chem.*, 1991, 307, 169–182.

**Table S4.** $-\Delta_{solv}G^0$(anion) $-\Delta_{solv}G^0$(neutral) (kcal·mol$^{-1}$) for chlorinated 1,4-benzoquinones ($BQ^{0/\bullet-}$) calculated at IEFPCM-B3LYP/6-31+G(d,p) level.

| Species | calcd | exp [a] |
|---|---|---|
| tetrachloro BQ | 50.1 | 49.2 |
| 2,5-dichloro BQ | 52.8 | 52.4 |
| 2,6-dichloro BQ | 52.9 | 52.1 |

[a] T. Heinis, S. Chowdhury, S. L. Scott and P. Kebarle, *J. Am. Chem. Soc.*, 1988, 110, 400–407.

Geometries in the gas-phase unless stated otherwise

**Table S5.** Optimised Cartesian coordinates (Å) for $C_6Cl_6$ obtained from B3LYP/6-31+G(d) 5d calculations

| | | | |
|---|---|---|---|
| C | -0.00000000 | 0.00000000 | 1.40534881 |
| C | -0.00000000 | 1.21706365 | 0.70267157 |
| C | 0.00000000 | 1.21706365 | -0.70267157 |
| C | 0.00000000 | -0.00000000 | -1.40534881 |
| C | -0.00000000 | -1.21706365 | -0.70267157 |
| C | -0.00000000 | -1.21706365 | 0.70267157 |
| Cl | 0.00000000 | 2.71884080 | 1.56968605 |
| Cl | 0.00000000 | 2.71884080 | -1.56968605 |
| Cl | 0.00000000 | 0.00000000 | -3.13944453 |
| Cl | -0.00000000 | -2.71884080 | -1.56968605 |
| Cl | -0.00000000 | -2.71884080 | 1.56968605 |
| Cl | -0.00000000 | 0.00000000 | 3.13944453 |

**Table S6.** Optimised Cartesian coordinates (Å) for $C_6Cl_6^{\bullet-}$ obtained from B3LYP/6-31+G(d) 5d calculations

| | | | |
|---|---|---|---|
| C | -1.20943810 | 0.69166370 | -0.04242136 |
| C | 0.00000000 | 1.39245919 | 0.06799570 |
| C | 1.20943810 | 0.69166370 | -0.04242136 |
| C | 1.20943810 | -0.69166370 | -0.04242136 |
| C | -0.00000000 | -1.39245919 | 0.06799570 |
| C | -1.20943810 | -0.69166370 | -0.04242136 |
| Cl | -0.00000000 | -3.09984104 | 0.66158485 |
| Cl | 2.73935197 | -1.60787197 | -0.32781941 |
| Cl | 2.73935197 | 1.60787197 | -0.32781941 |
| Cl | 0.00000000 | 3.09984104 | 0.66158485 |
| Cl | -2.73935197 | 1.60787197 | -0.32781941 |
| Cl | -2.73935197 | -1.60787197 | -0.32781941 |

**Table S7.** Optimised Cartesian coordinates (Å) for $C_6Cl_6$ obtained from B2PLYPD/aug-cc-pVTZ calculations

| | | | |
|---|---|---|---|
| C | -0.00000000 | -0.00000000 | 1.39947168 |
| C | 0.00000000 | 1.21197579 | 0.69973566 |
| C | 0.00000000 | 1.21197579 | -0.69973566 |
| C | 0.00000000 | 0.00000000 | -1.39947168 |
| C | -0.00000000 | -1.21197579 | -0.69973566 |
| C | -0.00000000 | -1.21197579 | 0.69973566 |
| Cl | 0.00000000 | 2.70475795 | 1.56158645 |
| Cl | 0.00000000 | 2.70475795 | -1.56158645 |
| Cl | 0.00000000 | 0.00000000 | -3.12318822 |
| Cl | -0.00000000 | -2.70475795 | -1.56158645 |
| Cl | -0.00000000 | -2.70475795 | 1.56158645 |
| Cl | -0.00000000 | -0.00000000 | 3.12318822 |

**Table S8.** Optimised Cartesian coordinates (Å) for $C_6Cl_6^{\bullet-}$ obtained from B2PLYPD/aug-cc-pVTZ calculations

| | | | |
|---|---|---|---|
| C | -1.20522767 | 0.68961023 | -0.04140058 |
| C | -0.00000000 | 1.38707153 | 0.07297029 |
| C | 1.20522767 | 0.68961023 | -0.04140058 |
| C | 1.20522767 | -0.68961023 | -0.04140058 |
| C | 0.00000000 | -1.38707153 | 0.07297029 |
| C | -1.20522767 | -0.68961023 | -0.04140058 |
| Cl | 0.00000000 | -3.06655384 | 0.69444743 |
| Cl | 2.71653791 | -1.59721041 | -0.34548886 |
| Cl | 2.71653791 | 1.59721041 | -0.34548886 |
| Cl | -0.00000000 | 3.06655384 | 0.69444743 |
| Cl | -2.71653791 | 1.59721041 | -0.34548886 |
| Cl | -2.71653791 | -1.59721041 | -0.34548886 |

**Table S9.** Optimised Cartesian coordinates (Å) for $C_6Cl_5OMe$ obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | -0.02391644 | -0.71977512 | 1.21802546 |
| C | -0.12177380 | 0.68025778 | 1.21183459 |
| C | -0.16688513 | 1.38956055 | 0.00000000 |
| C | -0.12177380 | 0.68025778 | -1.21183459 |
| C | -0.02391644 | -0.71977512 | -1.21802546 |
| C | 0.02811046 | -1.42091323 | -0.00000000 |
| O | -0.33296351 | 2.73823820 | 0.00000000 |
| C | 0.87358984 | 3.52561421 | 0.00000000 |
| H | 0.54549240 | 4.56545806 | 0.00000000 |
| H | 1.46655095 | 3.32484643 | -0.89834331 |
| H | 1.46655095 | 3.32484643 | 0.89834331 |
| Cl | -0.20872390 | 1.57926997 | 2.69637498 |
| Cl | 0.03017337 | -1.57982611 | 2.72434687 |
| Cl | 0.15266021 | -3.15255935 | -0.00000000 |
| Cl | 0.03017337 | -1.57982611 | -2.72434687 |
| Cl | -0.20872390 | 1.57926997 | -2.69637498 |

**Table S10.** Optimised Cartesian coordinates (Å) for $Cl^-...C_6Cl_4OMe^\bullet$ obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | 0.23233290 | 0.66224644 | 1.19802080 |
| C | 0.16034207 | -0.73681623 | 1.21048444 |
| C | 0.10252255 | -1.44906248 | -0.00000000 |
| C | 0.16034207 | -0.73681623 | -1.21048444 |
| C | 0.23233290 | 0.66224644 | -1.19802080 |
| C | 0.23757015 | 1.34725972 | 0.00000000 |
| O | 0.04839120 | -2.82277152 | -0.00000000 |
| C | -1.27411068 | -3.36708035 | -0.00000000 |
| H | -1.15627163 | -4.45362355 | -0.00000000 |
| H | -1.82487491 | -3.05877829 | -0.89696713 |
| H | -1.82487491 | -3.05877829 | 0.89696713 |
| Cl | 0.16034207 | -1.66871799 | 2.71216957 |
| Cl | 0.36223717 | 1.54249370 | 2.73254967 |
| Cl | -0.73275260 | 3.47959497 | 0.00000000 |
| Cl | 0.36223717 | 1.54249370 | -2.73254967 |
| Cl | 0.16034207 | -1.66871799 | -2.71216957 |

**Table S11.** Optimised Cartesian coordinates (Å) for $Cl^-...C_6Cl_4OMe^\bullet$ in DMF obtained from IEFPCM-B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | -0.20389552 | -0.61854479 | 1.20538740 |
| C | -0.14657709 | 0.78523698 | 1.21489787 |
| C | -0.10365474 | 1.49439692 | -0.00000000 |
| C | -0.14657709 | 0.78523698 | -1.21489787 |
| C | -0.20389552 | -0.61854479 | -1.20538740 |
| C | -0.21796549 | -1.28346368 | 0.00000000 |
| O | -0.09771286 | 2.85988503 | -0.00000000 |
| C | 1.21000605 | 3.47521154 | -0.00000000 |
| H | 1.03244558 | 4.55097822 | -0.00000000 |
| H | 1.76854710 | 3.19099757 | -0.89696227 |
| H | 1.76854710 | 3.19099757 | 0.89696227 |
| Cl | -0.14657709 | 1.69781184 | 2.70793728 |
| Cl | -0.28585381 | -1.51054885 | 2.72159467 |
| Cl | 0.57589237 | -3.78212766 | 0.00000000 |
| Cl | -0.28585381 | -1.51054885 | -2.72159467 |
| Cl | -0.14657709 | 1.69781184 | -2.70793728 |

**Table S12.** Optimised Cartesian coordinates (Å) for $C_6Cl_5OMe^{\bullet-}$ obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | 1.29557354 | -0.59808304 | -0.06873044 |
| C | 0.14293788 | -1.41153107 | -0.04457697 |
| C | -1.12721285 | -0.85103374 | -0.12382321 |
| C | -1.23983203 | 0.54910313 | -0.16040046 |
| C | -0.10526395 | 1.35635846 | 0.02198451 |
| C | 1.15308657 | 0.78343161 | 0.03756986 |
| O | -2.23422722 | -1.67175001 | -0.18195368 |
| C | -3.10474220 | -1.60360972 | 0.94819573 |
| H | -3.93219628 | -2.28545947 | 0.73491925 |
| H | -3.49448151 | -0.59041624 | 1.09477781 |
| H | -2.58441239 | -1.93503848 | 1.85679704 |
| Cl | 0.28818867 | -3.16995126 | 0.31577384 |
| Cl | 2.87405902 | -1.32385233 | -0.55667645 |
| Cl | 2.63358378 | 1.82306128 | 0.25902490 |
| Cl | -0.33821642 | 3.09430173 | 0.51272683 |
| Cl | -2.76363704 | 1.27274061 | -0.87744788 |

**Table S13.** Optimised Cartesian coordinates (Å) for $C_6Cl_4OMe^{\bullet}$ obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | -0.11493729 | -1.13716880 | 1.22610932 |
| C | -0.07568602 | 0.27045850 | 1.22400255 |
| C | -0.05253562 | 0.97242990 | 0.00000000 |
| C | -0.07568602 | 0.27045850 | -1.22400255 |
| C | -0.11493729 | -1.13716880 | -1.22610932 |
| C | -0.12913927 | -1.74846376 | -0.00000000 |
| O | -0.08531147 | 2.33231341 | 0.00000000 |
| C | 1.19374528 | 2.99460944 | 0.00000000 |
| H | 0.97218270 | 4.06229276 | 0.00000000 |
| H | 1.76393866 | 2.73531138 | -0.89819223 |
| H | 1.76393866 | 2.73531138 | 0.89819223 |
| Cl | -0.07568602 | 1.16645388 | 2.71276355 |
| Cl | -0.14791724 | -2.08122896 | 2.68770552 |
| Cl | -0.14791724 | -2.08122896 | -2.68770552 |
| Cl | -0.07568602 | 1.16645388 | -2.71276355 |

**Table S14.** Optimised Cartesian coordinates (Å) for 2,4-D obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | -0.50848095 | 2.86302027 | 0.15752398 |
| Cl | -3.93160147 | -1.34922283 | 0.13975714 |
| C | 0.29660606 | 0.29080315 | -0.30600268 |
| C | -0.78395632 | 1.14701355 | -0.02087965 |
| C | -2.07669185 | 0.64829959 | 0.11724038 |
| C | -2.30052619 | -0.72119669 | -0.03203898 |
| C | -1.24821431 | -1.58775216 | -0.31240431 |
| C | 0.04601424 | -1.07839444 | -0.44514797 |
| C | 2.63301553 | 0.11452589 | -0.83140815 |
| C | 3.24414710 | -0.69207988 | 0.31072593 |
| H | 4.69986828 | -1.86350596 | 0.61399823 |
| H | -2.89463241 | 1.32427797 | 0.33614530 |
| H | -1.42728718 | -2.65170291 | -0.41890328 |
| H | 0.85571822 | -1.77055805 | -0.64246165 |
| H | 2.40509024 | -0.55276093 | -1.67267192 |
| H | 3.38458812 | 0.83118259 | -1.17612554 |
| O | 2.85819760 | -0.71966157 | 1.45387909 |
| O | 4.31988871 | -1.38236890 | -0.14102860 |
| O | 1.52137497 | 0.87968008 | -0.43463394 |

**Table S15.** Optimised Cartesian coordinates (Å) for [2,4-D – 2-Cl]• obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | -3.89188434 | -1.43618164 | 0.16565154 |
| C | 0.36290453 | 0.14136035 | -0.42313398 |
| C | -0.73371761 | 0.96489395 | -0.22187202 |
| C | -2.03073492 | 0.56382192 | -0.03711154 |
| C | -2.25925971 | -0.82446415 | -0.05891873 |
| C | -1.20433871 | -1.71292132 | -0.25404033 |
| C | 0.10205625 | -1.23798026 | -0.43278059 |
| C | 2.69788725 | -0.06643317 | -0.92095613 |
| C | 3.30770271 | -0.75772332 | 0.29517662 |
| H | 4.75508171 | -1.90428939 | 0.71209433 |
| H | -2.84507736 | 1.26471045 | 0.11644552 |
| H | -1.39227458 | -2.78076595 | -0.26005113 |
| H | 0.90157996 | -1.96018640 | -0.56100293 |
| H | 2.47164705 | -0.81416029 | -1.69235888 |
| H | 3.45167262 | 0.61112750 | -1.33356386 |
| O | 2.92824247 | -0.66517574 | 1.43716920 |
| O | 4.37621118 | -1.50026763 | -0.08733394 |
| O | 1.58490441 | 0.73327223 | -0.60396146 |

**Table S16.** Optimised Cartesian coordinates (Å) for 2,4,5-T obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.49583023 | 0.00000000 |
| C | 1.40298201 | 0.35490965 | 0.00000000 |
| C | 1.98159988 | -0.90773674 | 0.00000000 |
| C | 1.18620446 | -2.05911985 | 0.00000000 |
| C | -0.20458031 | -1.92749346 | 0.00000000 |
| C | -0.79116936 | -0.65644517 | 0.00000000 |
| O | -0.48864760 | 1.76353517 | 0.00000000 |
| C | -1.88657031 | 1.94658518 | 0.00000000 |
| C | -2.17860366 | 3.43861814 | 0.00000000 |
| O | -1.37377073 | 4.33505170 | 0.00000000 |
| O | -3.52225229 | 3.62406536 | 0.00000000 |
| Cl | 2.41919959 | 1.77014207 | 0.00000000 |
| Cl | 1.96774636 | -3.61924199 | 0.00000000 |
| Cl | -1.25616867 | -3.32053702 | 0.00000000 |
| H | -2.35456431 | 1.50175431 | 0.88916335 |
| H | -2.35456431 | 1.50175431 | -0.88916335 |
| H | -3.68561688 | 4.58245411 | 0.00000000 |
| H | 3.06105828 | -1.00210431 | 0.00000000 |
| H | -1.87133789 | -0.59213614 | 0.00000000 |

**Table S17.** Optimised Cartesian coordinates (Å) for [2,4,5-T – 5-Cl]• obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| C | -0.09552207 | -0.16868986 | 0.00000000 |
| C | 0.78554377 | 0.93581733 | 0.00000000 |
| C | 2.16814375 | 0.76294347 | 0.00000000 |
| C | 2.70998297 | -0.53160833 | 0.00000000 |
| C | 1.82247533 | -1.57617552 | 0.00000000 |
| C | 0.44956364 | -1.46778705 | 0.00000000 |
| O | -1.42583529 | 0.10836882 | 0.00000000 |
| C | -2.33488550 | -0.96875611 | 0.00000000 |
| C | -3.74876460 | -0.40994278 | 0.00000000 |
| O | -4.06992934 | 0.75112635 | 0.00000000 |
| O | -4.62983533 | -1.44156263 | 0.00000000 |
| Cl | 0.13130237 | 2.55374237 | 0.00000000 |
| Cl | 4.44384052 | -0.77795075 | 0.00000000 |
| H | -2.21282348 | -1.60278078 | 0.88924498 |
| H | -2.21282348 | -1.60278078 | -0.88924498 |
| H | -5.52481845 | -1.06184917 | 0.00000000 |
| H | 2.81976559 | 1.63030516 | 0.00000000 |
| H | -0.18115090 | -2.34961977 | 0.00000000 |

**Table S18.** Optimised Cartesian coordinates (Å) for 2,4-D adduct with a DMF molecule obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | -0.60125868 | 2.88575885 | -0.01271610 |
| Cl | -4.03445097 | -1.32001083 | -0.00686140 |
| C | 0.21323358 | 0.30057475 | -0.38346606 |
| C | -0.87504353 | 1.16450721 | -0.15178753 |
| C | -2.17278317 | 0.67328890 | -0.03566602 |
| C | -2.39596783 | -0.69921695 | -0.15266040 |
| C | -1.33858202 | -1.57481595 | -0.38083367 |
| C | -0.03997413 | -1.07222485 | -0.49279467 |
| C | 2.56931486 | 0.08702747 | -0.79035387 |
| C | 3.10171986 | -0.68720883 | 0.41624237 |
| H | 4.51769007 | -1.92461738 | 0.86873655 |
| H | -2.99438638 | 1.35701975 | 0.14154534 |
| H | -1.51769349 | -2.64088946 | -0.46481929 |
| H | 0.77335497 | -1.76987318 | -0.65126990 |
| H | 2.38579111 | -0.60384583 | -1.62256907 |
| H | 3.34588215 | 0.78725587 | -1.11102546 |
| O | 2.63516320 | -0.60657766 | 1.53896138 |
| O | 4.14190113 | -1.43403347 | 0.06466301 |
| O | 1.43839849 | 0.88055545 | -0.49793586 |
| C | 4.54800263 | -2.47959799 | 3.22600009 |
| O | 5.11441499 | -2.69592308 | 2.14023770 |
| N | 4.92023752 | -3.02834895 | 4.39725939 |
| H | 3.68295080 | -1.80428332 | 3.28310880 |
| C | 4.20789820 | -2.72795010 | 5.63217999 |
| H | 3.38984789 | -2.03417363 | 5.42710862 |
| H | 3.79194226 | -3.64389320 | 6.06797105 |
| H | 4.88377556 | -2.26913608 | 6.36331393 |
| C | 6.05260375 | -3.94444300 | 4.47570979 |
| H | 6.47574356 | -4.06394369 | 3.47875846 |
| H | 6.81598813 | -3.54375867 | 5.15259486 |
| H | 5.72405077 | -4.91932545 | 4.85409183 |

**Table S19.** Optimised Cartesian coordinates (Å) for H-bonded dimer of 2,4-D obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | -0.54595861 | -1.17290964 | -1.54133255 |
| Cl | 3.28101486 | -4.92786584 | -0.69583222 |
| C | -0.85682601 | -3.79970464 | -2.23495943 |
| C | -0.00844182 | -2.83032933 | -1.66707524 |
| C | 1.25665150 | -3.17243840 | -1.19656027 |
| C | 1.68600693 | -4.49726947 | -1.29024502 |
| C | 0.86565593 | -5.47307174 | -1.84854824 |
| C | -0.40118456 | -5.11965503 | -2.32061233 |
| C | -3.01160949 | -4.28305917 | -3.17469758 |
| C | -2.73980659 | -4.66996355 | -4.62432028 |
| H | -3.44528890 | -5.78135569 | -6.02673656 |
| H | 1.89395886 | -2.41153239 | -0.76206457 |
| H | 1.20670419 | -6.49949102 | -1.92318114 |
| H | -1.01985842 | -5.89072594 | -2.76427600 |
| H | -3.09776439 | -5.19127778 | -2.56509738 |
| H | -3.98221486 | -3.77811936 | -3.14527695 |
| O | -1.82721414 | -4.18887143 | -5.28932130 |
| O | -3.61440561 | -5.55680144 | -5.06038586 |
| O | -2.08170066 | -3.36549734 | -2.65379437 |
| O | -1.33219810 | -4.74504173 | -7.83002403 |
| O | -3.11939826 | -6.11296102 | -7.60109274 |
| Cl | -4.40064625 | -9.12893086 | -11.34908158 |
| Cl | -8.22759273 | -5.37395922 | -12.19463559 |
| C | -4.08977163 | -6.50213395 | -10.65546504 |
| C | -4.93815561 | -7.47150771 | -11.22335224 |
| C | -6.20324299 | -7.12939457 | -11.69388019 |
| C | -6.63259244 | -5.80456080 | -11.60020608 |

| | | | |
|---|---|---|---|
| C | -5.81224139 | -4.82875993 | -11.04190048 |
| C | -4.54540703 | -5.18218079 | -10.56982304 |
| C | -1.93499322 | -6.01878551 | -9.71571175 |
| C | -2.20680029 | -5.63187577 | -8.26609111 |
| H | -1.50131871 | -4.52048252 | -6.86367515 |
| H | -6.84055031 | -7.89029949 | -12.12837784 |
| H | -6.15328501 | -3.80233849 | -10.96727596 |
| H | -3.92673321 | -4.41111084 | -10.12615772 |
| H | -1.84883259 | -5.11056908 | -10.32531447 |
| H | -0.96438959 | -6.52372898 | -9.74512671 |
| O | -2.86490306 | -6.93634547 | -10.23661664 |

**Table S20.** Optimised Cartesian coordinates (Å) for 2,4,5-T adduct with a DMF molecule obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | 1.17462219 | 3.00998663 | 0.00000000 |
| Cl | -3.94305156 | 4.75952010 | 0.00000000 |
| C | -0.96161196 | 1.30123721 | 0.00000000 |
| C | -0.53052352 | 2.64477551 | 0.00000000 |
| C | -1.45369920 | 3.68212719 | 0.00000000 |
| C | -2.82749390 | 3.41607507 | 0.00000000 |
| C | -3.26433166 | 2.08932948 | 0.00000000 |
| C | -2.33640451 | 1.04166745 | 0.00000000 |
| C | -0.39373159 | -1.01154959 | 0.00000000 |
| C | 0.84927222 | -1.89399923 | 0.00000000 |
| H | 1.30164283 | -3.77440335 | 0.00000000 |
| H | -1.10651555 | 4.70857348 | 0.00000000 |
| H | -2.71001764 | 0.02630460 | 0.00000000 |
| H | -0.99100579 | -1.25419042 | 0.88910531 |
| H | -0.99100579 | -1.25419042 | -0.88910531 |
| O | 1.99346895 | -1.48184639 | 0.00000000 |
| O | 0.48612221 | -3.17220174 | 0.00000000 |
| O | 0.00000000 | 0.34747835 | 0.00000000 |
| C | 3.69228517 | -4.15056553 | 0.00000000 |
| O | 2.59033389 | -4.72672071 | 0.00000000 |
| N | 4.87916637 | -4.78559181 | 0.00000000 |
| H | 3.75205588 | -3.05326533 | 0.00000000 |
| C | 6.13269128 | -4.04325474 | 0.00000000 |
| H | 5.92662061 | -2.97081248 | 0.00000000 |
| H | 6.72397367 | -4.28822259 | 0.89012218 |
| H | 6.72397367 | -4.28822259 | -0.89012218 |
| C | 4.95599938 | -6.24212773 | 0.00000000 |
| H | 3.94394039 | -6.64585224 | 0.00000000 |
| H | 5.49047886 | -6.59202095 | -0.89075704 |
| H | 5.49047886 | -6.59202095 | 0.89075704 |
| Cl | -4.96350564 | 1.68587559 | 0.00000000 |

**Table S21.** Optimised Cartesian coordinates (Å) for H-bonded dimer of 2,4,5-T obtained from B3LYP/6-31+G(d,p) 5d calculations

| | | | |
|---|---|---|---|
| Cl | -5.38703148 | -3.00545732 | 0.00000000 |
| Cl | -10.02253835 | -0.21973781 | 0.00000000 |
| Cl | -8.33083013 | 2.54039945 | 0.00000000 |
| O | -4.10831837 | -0.39317772 | 0.00000000 |
| O | -1.45100815 | -0.75764929 | 0.00000000 |
| O | -1.09531700 | 1.47641201 | 0.00000000 |
| C | -5.46210131 | -0.27180820 | 0.00000000 |
| C | -6.20799257 | -1.46806527 | 0.00000000 |
| C | -7.59634788 | -1.42984442 | 0.00000000 |
| C | -8.27792468 | -0.20768046 | 0.00000000 |
| C | -7.54558073 | 0.98216908 | 0.00000000 |
| C | -6.14612376 | 0.94698755 | 0.00000000 |
| C | -3.32721059 | 0.78018394 | 0.00000000 |
| C | -1.85711296 | 0.39821560 | 0.00000000 |
| H | -8.15777345 | -2.35663092 | 0.00000000 |
| H | -3.51878127 | 1.39733827 | -0.88875868 |

| | | | |
|---|---|---|---|
| H | -3.51878127 | 1.39733827 | 0.88875868 |
| Cl | 5.38703148 | 3.00545732 | 0.00000000 |
| Cl | 10.02253835 | 0.21973781 | 0.00000000 |
| Cl | 8.33083013 | -2.54039945 | 0.00000000 |
| O | 4.10831837 | 0.39317772 | 0.00000000 |
| O | 1.45100815 | 0.75764929 | 0.00000000 |
| O | 1.09531700 | -1.47641201 | 0.00000000 |
| C | 5.46210131 | 0.27180820 | 0.00000000 |
| C | 6.20799257 | 1.46806527 | 0.00000000 |
| C | 7.59634788 | 1.42984442 | 0.00000000 |
| C | 8.27792468 | 0.20768046 | 0.00000000 |
| C | 7.54558073 | -0.98216908 | 0.00000000 |
| C | 6.14612376 | -0.94698755 | 0.00000000 |
| C | 3.32721059 | -0.78018394 | 0.00000000 |
| C | 1.85711296 | -0.39821560 | 0.00000000 |
| H | 8.15777345 | 2.35663092 | 0.00000000 |
| H | 3.51878127 | -1.39733827 | 0.88875868 |
| H | 3.51878127 | -1.39733827 | -0.88875868 |
| H | 5.61148175 | -1.88780249 | 0.00000000 |
| H | -5.61148175 | 1.88780249 | 0.00000000 |
| H | 0.12100221 | -1.22475505 | 0.00000000 |
| H | -0.12100221 | 1.22475505 | 0.00000000 |