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***Supplementary Material***

# New Insights into the Origin of the *cis*-Configuration Preferences in 1,2-Dihaloethenes: The Importance of the Bonding Orbital Deviations

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**Table S1**. G3MP2 calculated zero point energies, corrected electronic energies [$E_o=E_{el}+ZPE$], thermodynamic functions [$H$, $S$, $G$] and their corresponding differences [$\Delta ZPE$, $\Delta H$, $\Delta G$ (in kcal mol$^{-1}$) and $\Delta S$ (in cal mol$^{-1}$K$^{-1}$)] at 300 K for the *cis*- and *trans*-configurations of compounds **1-3**.

| | G3MP2 | | | | | | | | | | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H$ | $S$ | $G$ | $ZPE$ | $E_o$ | $\Delta H$ | $\Delta S$ | $\Delta G$ | $\Delta ZPE$ | $\Delta E_o$ | $\Delta E_o$ |
| **1**-*cis* | -276.740885 | 64.128 | -276.771379 | 0.036108 | -276.745722 | 0.00 | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 |
| **1**-*trans* | -276.739635 | 63.947 | -276.770043 | 0.035757 | -276.744577 | 0.78 | -0.181 | 0.84 | -0.22 | 0.72 | (1.08 ± 0.12)[a] |
| **2**-*cis* | -996.748379 | 69.184 | -996.781277 | 0.033277 | -996.753622 | 0.00 | 0.000 | 0.00 | 0.00 | 0.00 | 0.0 |
| **2**-*trans* | -996.747338 | 69.392 | -996.780335 | 0.032957 | -996.752839 | 0.91 | 0.208 | 0.59 | -0.20 | 0.49 | (0.72 ± 0.16)[a] |
| **3**-*cis* | -5222.897277 | 74.742 | -5222.932818 | 0.031971 | -5222.902856 | 0.00 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 |
| **3**-*trans* | -5222.896787 | 75.074 | -5222.932486 | 0.031696 | -5222.902684 | 0.31 | 0.332 | 0.21 | -0.17 | 0.11 | (0.25 ± 0.33)[a] |

[a] From gas chromatography, Ref. [4].

**Table S2**. CCSD(T)/6-311+G** calculated zero point energies, corrected electronic energies [$E_o$=$E_{el}$+*ZPE*], thermodynamic functions [*H*, *S*, *G*] and their corresponding differences [Δ*ZPE*, Δ*H*, Δ*G* (in kcal mol$^{-1}$) and Δ*S* (in cal mol$^{-1}$K$^{-1}$)] for the *cis*- and *trans*-configurations of compounds **1-3**.

| | CCSD(T)/6-311+G** | | | | | | | | | | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *H* | *S* | *G* | *ZPE* | $E_o$ | Δ*H* | Δ*S* | Δ*G* | Δ*ZPE* | Δ$E_o$ | Δ$E_o$ |
| **1**-*cis* | -276.491846 | 64.252 | -276.522374 | 0.036782 | -276.496690 | 0.00 | 0.000 | 0.00 | 0.005276 | 0.00 | 0.00 |
| **1**-*trans* | -276.491076 | 64.141 | -276.521552 | 0.036431 | -276.496033 | 0.48 | -0.111 | 0.52 | 0.004925 | 0.41 | (1.08 ± 0.12)[a] |
| **2**-*cis* | -996.479827 | 69.263 | -996.512736 | 0.034036 | -996.485077 | 0.00 | 0.000 | 0.00 | 0.004174 | 0.00 | 0.0 |
| **2**-*trans* | -996.479470 | 69.483 | -996.512483 | 0.033770 | -996.484963 | 0.22 | 0.220 | 0.16 | 0.003908 | 0.07 | (0.72 ± 0.16)[a] |
| **3**-*cis* | -5222.171049 | 74.807 | -5222.206592 | 0.032601 | -5222.176635 | 0.00 | 0.000 | 0.00 | 0.004151 | 0.00 | 0.00 |
| **3**-*trans* | -5222.171898 | 75.100 | -5222.207580 | 0.032381 | -5222.177780 | -0.53 | 0.293 | -0.62 | 0.003931 | -0.72 | (0.25 ± 0.33)[a] |

[a] From gas chromatography, Ref. [4].

**Table S3.** LC-ωPBE/6-311+G** calculated zero point energies, corrected electronic energies [$E_o$=$E_{el}$+*ZPE*], thermodynamic functions [*H*, *S*, *G*] and their corresponding differences [Δ*ZPE*, Δ*H*, Δ*G* (in kcal mol$^{-1}$) and Δ*S* (in cal mol$^{-1}$K$^{-1}$)] at 300 K for the *cis*- and *trans*-configurations of compounds **1-3**.

| | LC-ωPBE/6-311+G** | | | | | | | | | | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *ZPE* | $E_o$ | *H* | *S* | *G* | Δ*ZPE* | Δ$E_o$ | Δ*H* | Δ*S* | Δ*G* | Δ$E_o$ |
| **1**-*cis* | 0.037673 | -276.935966 | -276.931192 | 63.999 | -276.961600 | 0.00 | 0.00 | 0.00 | 0.000 | 0.00 | 0.00 |
| **1**-*trans* | 0.037268 | -276.935195 | -276.930302 | 63.886 | -276.960656 | -0.25 | 0.48 | 0.56 | -0.113 | 0.59 | (1.08 ± 0.12)[a] |
| **2**-*cis* | 0.035165 | -997.480930 | -997.475803 | 68.791 | -997.508488 | 0.00 | 0.00 | 0.00 | 0.000 | 0.00 | 0.0 |
| **2**-*trans* | 0.034794 | -997.480659 | -997.475279 | 68.969 | -997.508048 | -0.23 | 0.17 | 0.33 | 0.178 | 0.28 | (0.72 ± 0.16)[a] |
| **3**-*cis* | 0.033892 | -5224.838383 | -5224.832951 | 74.193 | -5224.868203 | 0.00 | 0.00 | 0.00 | 0.000 | 0.00 | 0.00 |
| **3**-*trans* | 0.033528 | -5224.839033 | -5224.833275 | 74.534 | -5224.868688 | -0.23 | -0.41 | -0.20 | 0.341 | -0.30 | (0.25 ± 0.33)[a] |

[a] From gas chromatography, Ref. [4].

**Table S4.** NBO-LC-ωPBE/6-311+G** calculated orbital occupancies (*e*) and orbital energies (*ε*, in a.u.) for the *cis*- and *trans*-configurations of compounds **1-3**.

| | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* |
| *ε* | | | | | | |
| $\sigma_{C-H}$ | -0.70496 | -0.70646 | -0.69573 | -0.70128 | -0.69328 | -0.70008 |
| $\sigma_{C-X}$ | -1.16131 | -1.15108 | -0.88813 | -0.88037 | -0.81937 | -0.81086 |
| $LP_3X$ | -0.54573 | -0.54849 | -0.44486 | -0.44927 | -0.41582 | -0.42043 |
| $\sigma^*_{C-X}$ | 0.38302 | 0.37549 | 0.27491 | 0.26798 | 0.21290 | 0.20532 |
| $\sigma^*_{C-H}$ | 0.48360 | 0.48338 | 0.50191 | 0.50268 | 0.51111 | 0.51216 |
| $\pi^*_{C=C}$ | 0.09133 | 0.09277 | 0.07644 | 0.07787 | 0.07821 | 0.07787 |
| $\Delta[\varepsilon(\pi^*_{C=C})-\varepsilon(LP_3X)]$ | 0.63706 | 0.64126 | 0.52130 | 0.52714 | 0.49403 | 0.4983 |
| $\Delta[\varepsilon(\sigma^*_{C-X})-\varepsilon(\sigma_{C-H})]$ | 1.08798 | 1.08195 | 0.97064 | 0.96926 | 0.90618 | 0.9054 |
| $\Delta[\varepsilon(\sigma^*_{C-X})-\varepsilon(\sigma_{C-X})]$ | 1.54433 | 1.52657 | 1.16304 | 1.14835 | 1.03227 | 1.01618 |
| *e* | | | | | | |
| $\sigma_{C-H}$ | 1.98285 | 1.98655 | 1.97488 | 1.98278 | 1.97217 | 1.98203 |
| $\sigma_{C-X}$ | 1.99652 | 1.99489 | 1.99158 | 1.98638 | 1.98872 | 1.98032 |
| $LP_3X$ | 1.92942 | 1.93537 | 1.92259 | 1.93194 | 1.92961 | 1.93929 |
| $\sigma^*_{C-X}$ | 0.01407 | 0.01156 | 0.01922 | 0.01807 | 0.02339 | 0.02329 |
| $\sigma^*_{C-H}$ | 0.01966 | 0.02073 | 0.02334 | 0.02359 | 0.02205 | 0.02206 |
| $\pi^*_{C=C}$ | 0.13383 | 0.12329 | 0.14841 | 0.13088 | 0.13523 | 0.11713 |

**Table S5**. LC-wPBE/6-311+G** calculated energies (in hartree) of HOMO ($\varepsilon_{HOMO}$), LUMO ($\varepsilon_{LUMO}$), $\varepsilon_{LUMO}$-$\varepsilon_{HOMO}$, ionization potential (*IP*), electron affinity (*EA*), global hardness ($\eta$), global electronegativity ($\chi$) for the *cis*- and *trans*-configurations of compounds **1-3**.

| | $\varepsilon_{HOMO}$ | $\varepsilon_{LUMO}$ | $\varepsilon_{LUMO}$-$\varepsilon_{HOMO}$ | *IP* | *EA* | $\eta$ | $\chi$ | $\Delta\eta$ | $\Delta\chi$ |
|---|---|---|---|---|---|---|---|---|---|
| **1**-*cis* | -0.38700 | 0.06048 | 0.44748 | 0.38700 | -0.06048 | 0.22374 | 0.16326 | 0.00000 | 0.00000 |
| **1**-*trans* | -0.38652 | 0.07354 | 0.46006 | 0.38652 | -0.07354 | 0.23003 | 0.15649 | 0.00629(3.95)[a] | -0.00677(-4.25)[a] |
| **2**-*cis* | -0.37318 | 0.06032 | 0.43350 | 0.37318 | -0.06032 | 0.21675 | 0.15643 | 0.00000 | 0.00000 |
| **2**-*trans* | -0.37258 | 0.05441 | 0.42699 | 0.37258 | -0.05441 | 0.21350 | 0.15909 | -0.00325(-2.04)[a] | 0.00266(1.67)[a] |
| **3**-*cis* | -0.36463 | 0.05276 | 0.41739 | 0.36463 | -0.05276 | 0.20870 | 0.15594 | 0.00000 | 0.00000 |
| **3**-*trans* | -0.36364 | 0.04875 | 0.41239 | 0.36364 | -0.04875 | 0.20620 | 0.15745 | -0.00250(-1.57) | 0.00151(0.95)[a] |

[a] Values are in kcal $mol^{-1}$.

**Table S6**. Δ-LC-wPBE/6-311+G** calculated ionization potential (*IP*), electron affinity (*EA*), global hardness ($\eta$), global electronegativity ($\chi$) (in hartree) for the *cis*- and *trans*-configurations of compounds **1-3**.

| | *IP* | *EA* | $\eta$ | $\chi$ | $\Delta\eta$ | $\Delta\chi$ |
|---|---|---|---|---|---|---|
| **1**-*cis* | 0.386502 | -0.082317 | 0.2344095 | 0.1520925 | 0.00000 | 0.00000 |
| **1**-*trans* | 0.386492 | -0.075502 | 0.230997 | 0.155495 | -0.003413(-2.14)[a] | 0.003403(2.14)[a] |
| **2**-*cis* | 0.366496 | -0.048189 | 0.2073425 | 0.15915 | 0.00000 | 0.00000 |
| **2**-*trans* | 0.366257 | -0.041098 | 0.2036775 | 0.16258 | -0.00367(-2.30)[a] | 0.00343(2.15)[a] |
| **3**-*cis* | 0.35724 | -0.03842 | 0.19782 | 0.15941 | 0.00000 | 0.00000 |
| **3**-*trans* | 0.35664 | -0.03205 | 0.19434 | 0.16230 | -0.003478(-2.18)[a] | 0.00289(1.81)[a] |

[a] Values are in kcal $mol^{-1}$.

**Table S7**. Δ-EOM-CCSD/6-311+G**//CCSD/6-311+G** calculated ionization potential (*IP*), electron affinity (*EA*), global hardness ($\eta$), global electronegativity ($\chi$) (in hartree) for the *cis- and trans*-configurations of compounds **1-3**.

| | *IP* | *EA* | $\eta$ | $\chi$ | $\Delta\eta$ | $\Delta\chi$ |
|---|---|---|---|---|---|---|
| **1**-*cis* | 0.3479042 | -0.1051421 | 0.22652315 | 0.1213810 | 0.00000 | 0.00000 |
| **1**-*trans* | 0.3472961 | -0.0966451 | 0.2219706 | 0.1253255 | -0.00455(-2.86)[a] | 0.00394(2.47)[a] |
| **2**-*cis* | 0.3299978 | -0.0722365 | 0.20111715 | 0.12888065 | 0.00000 | 0.00000 |
| **2**-*trans* | 0.3299993 | -0.065353 | 0.19767615 | 0.13232315 | -0.00344(-2.16)[a] | 0.00344(2.16)[a] |
| **3**-*cis* | 0.3252479 | -0.073224 | 0.19923595 | 0.12601195 | 0.00000 | 0.00000 |
| **3**-*trans* | 0.3254915 | -0.0548525 | 0.190172 | 0.1353195 | -0.00906(-5.69)[a] | 0.00931(5.84)[a] |

[a] Values are in kcal $mol^{-1}$.