# Supplementary Information

## Geometrical, electrical and energetic parameters of hetero-disubstituted cumulenes and polyynes in the presence and absence of the external electric field

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**Table S1** CC bond lengths (in Å) in unsubstituted and substituted cumulenes and polyynes using four different functionals

| | | | *cis*-cumulenes | | | | *trans*-cumulenes | | | | polyynes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | cumulene | cis-$NH_2$,OH | cis-$NO_2$,CN | cis-$NO_2$,$NH_2$ | cis-$NO_2$,OH | trans-$NH_2$,OH | trans-$NO_2$,CN | trans-$NO_2$,$NH_2$ | trans-$NO_2$,OH | polyyne | py-$NH_2$,OH | py-$NO_2$,CN | py-$NO_2$,$NH_2$ | py-$NO_2$,OH |
| B3LYP | 1-2 | 1.313 | 1.329 | 1.316 | 1.323 | 1.320 | 1.329 | 1.316 | 1.323 | 1.320 | 1.208 | 1.216 | 1.209 | 1.212 | 1.211 |
| | 2-3 | 1.266 | 1.260 | 1.260 | 1.256 | 1.258 | 1.260 | 1.260 | 1.256 | 1.258 | 1.350 | 1.344 | 1.342 | 1.339 | 1.341 |
| | 3-4 | 1.282 | 1.288 | 1.284 | 1.290 | 1.287 | 1.288 | 1.284 | 1.290 | 1.287 | 1.220 | 1.224 | 1.222 | 1.225 | 1.223 |
| | 4-5 | 1.269 | 1.266 | 1.265 | 1.260 | 1.263 | 1.266 | 1.265 | 1.260 | 1.263 | 1.340 | 1.337 | 1.335 | 1.332 | 1.334 |
| | 5-6 | 1.280 | 1.283 | 1.282 | 1.289 | 1.285 | 1.283 | 1.282 | 1.289 | 1.285 | 1.223 | 1.225 | 1.224 | 1.228 | 1.225 |
| | 6-7 | 1.269 | 1.268 | 1.264 | 1.259 | 1.263 | 1.268 | 1.264 | 1.259 | 1.263 | 1.340 | 1.339 | 1.334 | 1.332 | 1.336 |
| | 7-8 | 1.282 | 1.285 | 1.285 | 1.294 | 1.288 | 1.285 | 1.285 | 1.294 | 1.288 | 1.220 | 1.222 | 1.223 | 1.226 | 1.222 |
| | 8-9 | 1.266 | 1.265 | 1.258 | 1.253 | 1.259 | 1.264 | 1.258 | 1.253 | 1.259 | 1.350 | 1.349 | 1.339 | 1.338 | 1.345 |
| | 9-10 | 1.313 | 1.321 | 1.326 | 1.336 | 1.325 | 1.321 | 1.326 | 1.336 | 1.325 | 1.208 | 1.209 | 1.217 | 1.218 | 1.209 |
| B3LYP-D3 | 1-2 | 1.313 | 1.329 | 1.316 | 1.323 | 1.320 | 1.329 | 1.316 | 1.323 | 1.320 | 1.208 | 1.216 | 1.209 | 1.212 | 1.210 |
| | 2-3 | 1.266 | 1.259 | 1.260 | 1.255 | 1.257 | 1.259 | 1.260 | 1.255 | 1.257 | 1.350 | 1.343 | 1.342 | 1.339 | 1.341 |
| | 3-4 | 1.282 | 1.288 | 1.284 | 1.290 | 1.287 | 1.288 | 1.284 | 1.290 | 1.287 | 1.220 | 1.224 | 1.222 | 1.225 | 1.223 |
| | 4-5 | 1.269 | 1.266 | 1.264 | 1.260 | 1.263 | 1.266 | 1.264 | 1.260 | 1.263 | 1.340 | 1.337 | 1.335 | 1.331 | 1.334 |
| | 5-6 | 1.280 | 1.283 | 1.282 | 1.289 | 1.284 | 1.283 | 1.282 | 1.289 | 1.284 | 1.223 | 1.225 | 1.224 | 1.227 | 1.225 |
| | 6-7 | 1.269 | 1.268 | 1.264 | 1.259 | 1.263 | 1.268 | 1.264 | 1.259 | 1.263 | 1.340 | 1.339 | 1.334 | 1.331 | 1.336 |
| | 7-8 | 1.282 | 1.285 | 1.285 | 1.294 | 1.287 | 1.285 | 1.285 | 1.294 | 1.287 | 1.220 | 1.222 | 1.223 | 1.226 | 1.222 |
| | 8-9 | 1.266 | 1.264 | 1.258 | 1.252 | 1.259 | 1.264 | 1.258 | 1.252 | 1.259 | 1.350 | 1.348 | 1.339 | 1.338 | 1.345 |
| | 9-10 | 1.313 | 1.321 | 1.325 | 1.336 | 1.325 | 1.321 | 1.325 | 1.336 | 1.325 | 1.208 | 1.209 | 1.216 | 1.218 | 1.209 |
| CAM-B3LYP | 1-2 | 1.305 | 1.321 | 1.307 | 1.314 | 1.311 | 1.321 | 1.307 | 1.314 | 1.311 | 1.199 | 1.205 | 1.197 | 1.199 | 1.198 |
| | 2-3 | 1.265 | 1.258 | 1.259 | 1.254 | 1.256 | 1.258 | 1.259 | 1.254 | 1.256 | 1.362 | 1.355 | 1.356 | 1.354 | 1.355 |
| | 3-4 | 1.277 | 1.283 | 1.278 | 1.285 | 1.281 | 1.283 | 1.278 | 1.285 | 1.281 | 1.206 | 1.210 | 1.207 | 1.209 | 1.208 |
| | 4-5 | 1.266 | 1.264 | 1.263 | 1.257 | 1.261 | 1.264 | 1.263 | 1.257 | 1.261 | 1.353 | 1.352 | 1.351 | 1.349 | 1.350 |
| | 5-6 | 1.275 | 1.278 | 1.276 | 1.284 | 1.279 | 1.278 | 1.276 | 1.284 | 1.279 | 1.208 | 1.210 | 1.208 | 1.211 | 1.209 |
| | 6-7 | 1.266 | 1.266 | 1.263 | 1.256 | 1.261 | 1.266 | 1.263 | 1.256 | 1.261 | 1.353 | 1.353 | 1.351 | 1.348 | 1.351 |
| | 7-8 | 1.277 | 1.280 | 1.279 | 1.289 | 1.282 | 1.280 | 1.279 | 1.289 | 1.282 | 1.206 | 1.208 | 1.208 | 1.211 | 1.208 |
| | 8-9 | 1.265 | 1.263 | 1.258 | 1.250 | 1.257 | 1.263 | 1.258 | 1.250 | 1.257 | 1.362 | 1.360 | 1.353 | 1.351 | 1.357 |
| | 9-10 | 1.305 | 1.313 | 1.315 | 1.329 | 1.317 | 1.313 | 1.315 | 1.329 | 1.317 | 1.199 | 1.199 | 1.203 | 1.206 | 1.199 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ωB97XD | 1-2 | 1.306 | 1.322 | 1.308 | 1.315 | 1.311 | 1.322 | 1.308 | 1.314 | 1.311 | 1.201 | 1.207 | 1.199 | 1.200 | 1.200 |
| | 2-3 | 1.267 | 1.260 | 1.261 | 1.257 | 1.259 | 1.260 | 1.261 | 1.257 | 1.259 | 1.363 | 1.357 | 1.358 | 1.356 | 1.357 |
| | 3-4 | 1.278 | 1.283 | 1.278 | 1.285 | 1.281 | 1.283 | 1.278 | 1.285 | 1.281 | 1.208 | 1.211 | 1.208 | 1.210 | 1.209 |
| | 4-5 | 1.269 | 1.267 | 1.266 | 1.260 | 1.263 | 1.267 | 1.266 | 1.261 | 1.264 | 1.355 | 1.354 | 1.353 | 1.351 | 1.353 |
| | 5-6 | 1.276 | 1.279 | 1.276 | 1.285 | 1.280 | 1.279 | 1.276 | 1.285 | 1.280 | 1.210 | 1.212 | 1.210 | 1.212 | 1.211 |
| | 6-7 | 1.269 | 1.268 | 1.266 | 1.259 | 1.263 | 1.268 | 1.266 | 1.259 | 1.263 | 1.355 | 1.355 | 1.353 | 1.351 | 1.353 |
| | 7-8 | 1.278 | 1.280 | 1.279 | 1.290 | 1.283 | 1.280 | 1.279 | 1.290 | 1.283 | 1.208 | 1.210 | 1.209 | 1.212 | 1.210 |
| | 8-9 | 1.267 | 1.265 | 1.261 | 1.252 | 1.259 | 1.265 | 1.261 | 1.253 | 1.259 | 1.363 | 1.361 | 1.355 | 1.353 | 1.358 |
| | 9-10 | 1.306 | 1.315 | 1.316 | 1.330 | 1.319 | 1.315 | 1.316 | 1.330 | 1.319 | 1.201 | 1.201 | 1.205 | 1.208 | 1.201 |

**Table S2** Components (x, y, z) of dipole moment vector **μ** and its length (total) in D (debye) in unsubstituted and substituted cumulenes and polyynes using four different functionals

| | | | *cis*-cumulenes | | | | *trans*-cumulenes | | | | polyynes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | cumu-lene | cis-$NH_2$,OH | cis-$NO_2$,CN | cis-$NO_2$,NH2 | cis-$NO_2$,OH | trans-$NH_2$,OH | trans-$NO_2$,CN | trans-$NO_2$,NH2 | trans-$NO_2$,OH | polyyne | py-$NH_2$,OH | py-$NO_2$,CN | py-$NO_2$,$NH_2$ | py-$NO_2$,OH |
| B3LYP | $\mu_x$ | 0.000 | -4.932 | 1.951 | 15.689 | 9.332 | -4.944 | 1.920 | 15.659 | 9.297 | 0.000 | -1.880 | 0.335 | 12.963 | 10.191 |
| | $\mu_y$ | 0.000 | -1.549 | 5.812 | 2.227 | 2.475 | -0.490 | 0.133 | 4.749 | 4.034 | 0.000 | -0.799 | 0.000 | -0.001 | 1.520 |
| | $\mu_z$ | 0.000 | 0.619 | 0.000 | -0.001 | 0.000 | 0.612 | 0.000 | -0.001 | 0.000 | 0.000 | 0.014 | 0.000 | -0.484 | -0.032 |
| | $\mu_{total}$ | 0.000 | 5.207 | 6.131 | 15.846 | 9.655 | 5.006 | 1.924 | 16.363 | 10.134 | 0.000 | 2.043 | 0.335 | 12.972 | 10.304 |
| B3LYP-D3 | $\mu_x$ | 0.000 | -4.927 | 1.939 | 15.633 | 9.279 | -4.940 | 1.900 | 15.611 | 9.254 | 0.000 | -1.885 | 0.328 | 12.953 | 10.179 |
| | $\mu_y$ | 0.000 | -1.566 | 5.848 | 2.223 | 2.487 | -0.502 | 0.133 | 4.756 | 4.041 | 0.000 | -0.800 | 0.000 | 0.000 | 1.522 |
| | $\mu_z$ | 0.000 | 0.618 | 0.001 | -0.002 | 0.000 | 0.608 | 0.000 | -0.002 | 0.000 | 0.000 | 0.014 | 0.000 | -0.490 | -0.032 |
| | $\mu_{total}$ | 0.000 | 5.206 | 6.161 | 15.790 | 9.606 | 5.003 | 1.904 | 16.319 | 10.098 | 0.000 | 2.047 | 0.328 | 12.963 | 10.292 |
| CAM-B3LYP | $\mu_x$ | 0.000 | -5.004 | 1.744 | 15.458 | 9.024 | -5.024 | 1.716 | 15.436 | 9.001 | 0.000 | -1.703 | 0.062 | 10.882 | 8.703 |
| | $\mu_y$ | 0.000 | -1.511 | 5.897 | 2.205 | 2.458 | -0.486 | 0.040 | 4.640 | 3.960 | 0.000 | -0.802 | 0.001 | -0.001 | 1.549 |
| | $\mu_z$ | 0.000 | 0.592 | 0.001 | -0.002 | -0.001 | 0.580 | 0.000 | -0.002 | 0.000 | 0.000 | 0.012 | 0.000 | -0.613 | -0.027 |
| | $\mu_{total}$ | 0.000 | 5.260 | 6.150 | 15.614 | 9.353 | 5.081 | 1.717 | 16.118 | 9.833 | 0.000 | 1.882 | 0.062 | 10.899 | 8.840 |
| ωB97XD | $\mu_x$ | 0.000 | -4.760 | 1.562 | 15.228 | 8.917 | -4.775 | 1.536 | 15.212 | 8.899 | 0.000 | -1.584 | -0.111 | 10.538 | 8.538 |
| | $\mu_y$ | 0.000 | -1.550 | 5.812 | 2.083 | 2.346 | -0.449 | -0.031 | 4.567 | 3.899 | 0.000 | -0.716 | 0.000 | 0.002 | 1.532 |
| | $\mu_z$ | 0.000 | 0.651 | 0.000 | -0.002 | -0.001 | 0.643 | 0.000 | -0.002 | 0.000 | 0.000 | 0.011 | 0.000 | -0.712 | -0.027 |
| | $\mu_{total}$ | 0.000 | 5.048 | 6.019 | 15.370 | 9.221 | 4.839 | 1.536 | 15.883 | 9.715 | 0.000 | 1.738 | 0.111 | 10.562 | 8.675 |

**Table S3** Elements of polarizability tensor α in $Å^3$ in unsubstituted and substituted cumulenes and polyynes using four different functionals

| | | | *cis*-cumulenes | | | | *trans*-cumulenes | | | | polyynes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | cumu-lene | cis-$NH_2$,OH | cis-$NO_2$,CN | cis-$NO_2$,$NH_2$ | cis-$NO_2$,OH | trans-$NH_2$,OH | trans-$NO_2$,CN | trans-$NO_2$,$NH_2$ | trans-$NO_2$,OH | polyyne | py-$NH_2$,OH | py-$NO_2$,CN | py-$NO_2$,$NH_2$ | py-$NO_2$,OH |
| B3LYP | $\alpha_{xx}$ | 101.258 | 120.878 | 135.568 | 136.062 | 125.436 | 120.599 | 135.354 | 135.935 | 125.322 | 72.533 | 88.727 | 116.705 | 113.202 | 100.590 |
| | $\alpha_{yx}$ | 0.000 | 3.228 | -2.249 | 2.753 | 2.977 | 8.160 | 12.342 | 10.856 | 8.437 | 0.000 | 0.071 | -0.002 | 0.003 | 0.808 |
| | $\alpha_{yy}$ | 10.379 | 13.384 | 16.641 | 15.568 | 14.838 | 13.771 | 17.351 | 16.143 | 15.196 | 9.439 | 10.841 | 13.538 | 13.542 | 13.049 |
| | $\alpha_{zx}$ | 0.000 | -0.010 | 0.000 | -0.012 | 0.000 | -0.057 | 0.000 | -0.012 | -0.001 | 0.000 | 0.017 | 0.000 | -0.614 | -0.284 |
| | $\alpha_{zy}$ | 0.000 | 0.007 | 0.000 | -0.002 | 0.000 | 0.003 | 0.000 | -0.001 | 0.000 | 0.000 | -0.001 | -0.078 | -0.004 | -0.003 |
| | $\alpha_{zz}$ | 9.995 | 11.267 | 11.761 | 11.669 | 11.125 | 11.268 | 11.757 | 11.671 | 11.124 | 9.439 | 10.799 | 11.323 | 11.215 | 10.688 |
| | Tr(α) | 40.544 | 48.510 | 54.656 | 54.433 | 50.467 | 48.546 | 54.820 | 54.583 | 50.548 | 30.471 | 36.789 | 47.189 | 45.986 | 41.442 |
| B3LYP-D3 | $\alpha_{xx}$ | 101.231 | 120.803 | 135.250 | 135.862 | 125.261 | 120.549 | 135.105 | 135.779 | 125.193 | 72.533 | 88.703 | 116.685 | 113.171 | 100.571 |
| | $\alpha_{yx}$ | 0.000 | 3.219 | -2.284 | 2.733 | 2.939 | 8.105 | 12.225 | 10.773 | 8.354 | 0.000 | 0.085 | -0.001 | 0.001 | 0.798 |
| | $\alpha_{yy}$ | 10.378 | 13.402 | 16.697 | 15.600 | 14.868 | 13.774 | 17.362 | 16.148 | 15.200 | 9.439 | 10.840 | 13.537 | 13.542 | 13.049 |
| | $\alpha_{zx}$ | 0.000 | -0.012 | 0.000 | -0.012 | 0.000 | -0.059 | 0.000 | -0.011 | -0.002 | 0.000 | 0.019 | 0.000 | -0.607 | -0.284 |
| | $\alpha_{zy}$ | 0.000 | 0.007 | 0.000 | -0.002 | 0.000 | 0.002 | 0.000 | -0.001 | 0.000 | 0.000 | -0.001 | -0.078 | -0.004 | -0.003 |
| | $\alpha_{zz}$ | 9.994 | 11.267 | 11.759 | 11.669 | 11.125 | 11.268 | 11.755 | 11.670 | 11.124 | 9.439 | 10.797 | 11.322 | 11.213 | 10.687 |
| | Tr(α) | 40.534 | 48.490 | 54.569 | 54.377 | 50.418 | 48.530 | 54.740 | 54.532 | 50.506 | 30.471 | 36.780 | 47.181 | 45.975 | 41.436 |
| CAM-B3LYP | $\alpha_{xx}$ | 99.739 | 118.803 | 129.744 | 133.806 | 122.151 | 118.568 | 129.599 | 133.712 | 122.081 | 61.986 | 74.993 | 92.741 | 89.415 | 81.063 |
| | $\alpha_{yx}$ | 0.000 | 3.182 | -2.242 | 2.090 | 2.373 | 7.753 | 10.727 | 9.942 | 7.438 | 0.000 | 0.143 | -0.002 | 0.002 | 0.612 |
| | $\alpha_{yy}$ | 10.260 | 13.099 | 16.132 | 15.110 | 14.384 | 13.446 | 16.671 | 15.599 | 14.666 | 9.316 | 10.703 | 13.405 | 13.388 | 12.900 |
| | $\alpha_{zx}$ | 0.000 | -0.015 | -0.001 | -0.011 | 0.002 | -0.063 | -0.001 | -0.011 | 0.000 | 0.000 | 0.014 | 0.000 | -0.379 | -0.223 |
| | $\alpha_{zy}$ | 0.000 | 0.009 | 0.001 | -0.002 | 0.000 | 0.004 | 0.000 | -0.001 | 0.000 | 0.000 | -0.001 | -0.077 | -0.004 | -0.002 |
| | $\alpha_{zz}$ | 9.877 | 11.126 | 11.658 | 11.564 | 11.025 | 11.127 | 11.654 | 11.565 | 11.024 | 9.316 | 10.660 | 11.229 | 11.122 | 10.592 |
| | Tr(α) | 39.959 | 47.676 | 52.511 | 53.493 | 49.187 | 47.714 | 52.641 | 53.625 | 49.257 | 26.873 | 32.118 | 39.125 | 37.975 | 34.852 |
| ωB97XD | $\alpha_{xx}$ | 99.608 | 118.510 | 129.450 | 133.445 | 121.874 | 118.284 | 129.343 | 133.372 | 121.824 | 61.909 | 74.770 | 92.301 | 88.168 | 80.488 |
| | $\alpha_{yx}$ | 0.000 | 3.150 | -2.315 | 1.986 | 2.297 | 7.682 | 10.635 | 9.784 | 7.316 | 0.000 | 0.198 | -0.001 | 0.000 | 0.595 |
| | $\alpha_{yy}$ | 10.310 | 13.132 | 16.223 | 15.143 | 14.410 | 13.469 | 16.730 | 15.606 | 14.676 | 9.388 | 10.792 | 13.457 | 13.440 | 12.954 |
| | $\alpha_{zx}$ | 0.000 | 0.052 | 0.000 | -0.011 | 0.002 | 0.001 | -0.001 | -0.011 | 0.000 | 0.000 | 0.013 | 0.000 | -0.305 | -0.221 |
| | $\alpha_{zy}$ | 0.000 | 0.020 | 0.000 | -0.001 | 0.000 | 0.017 | 0.000 | -0.001 | 0.000 | 0.000 | -0.001 | -0.076 | 0.010 | -0.002 |
| | $\alpha_{zz}$ | 9.934 | 11.216 | 11.729 | 11.649 | 11.103 | 11.217 | 11.725 | 11.650 | 11.102 | 9.388 | 10.740 | 11.299 | 11.207 | 10.671 |
| | Tr(α) | 39.951 | 47.619 | 52.467 | 53.412 | 49.129 | 47.657 | 52.599 | 53.543 | 49.201 | 26.895 | 32.100 | 39.019 | 37.605 | 34.704 |

**Table S4** HOMO-LUMO gap energies (in eV) in unsubstituted and substituted cumulenes and polyynes using four different functionals

| | | *cis*-cumulenes | | | | *trans*-cumulenes | | | | polyynes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | cumu-lene | cis-$NH_2$,OH | cis-$NO_2$,CN | cis-$NO_2$,$NH_2$ | cis-$NO_2$,OH | trans-$NH_2$,OH | trans-$NO_2$,CN | trans-$NO_2$,$NH_2$ | trans-$NO_2$,OH | polyyne | py-$NH_2$,OH | py-$NO_2$,CN | py-$NO_2$,$NH_2$ | py-$NO_2$,OH |
| B3LYP | 2.71 | 2.43 | 2.37 | 2.27 | 2.40 | 2.43 | 2.37 | 2.27 | 2.40 | 3.87 | 3.56 | 3.09 | 2.84 | 3.10 |
| B3LYP-D3 | 2.71 | 2.43 | 2.37 | 2.27 | 2.40 | 2.43 | 2.37 | 2.27 | 2.40 | 3.87 | 3.56 | 3.09 | 2.84 | 3.09 |
| CAM-B3LYP | 4.86 | 4.52 | 4.48 | 4.26 | 4.46 | 4.52 | 4.48 | 4.26 | 4.46 | 6.55 | 6.19 | 5.80 | 5.30 | 5.65 |
| ωB97XD | 5.90 | 5.55 | 5.52 | 5.28 | 5.50 | 5.55 | 5.52 | 5.28 | 5.50 | 7.61 | 7.26 | 6.86 | 6.40 | 6.74 |

**Table S5** CC bond lengths (in Å) in unsubstituted and substituted cumulenes and polyynes in electric field *F*, computed using CAM-B3LYP/ aug-cc-pVTZ

| | *F* (V/Å) | 1-2 | 2-3 | 3-4 | 4-5 | 5-6 | 6-7 | 7-8 | 8-9 | 9-10 | mean | SD | HOMA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cumulene | -0.514 | 1.306 | 1.265 | 1.277 | 1.267 | 1.275 | 1.267 | 1.276 | 1.265 | 1.304 | 1.278 | 0.016 | -2.04 |
| | -0.257 | 1.305 | 1.265 | 1.277 | 1.267 | 1.275 | 1.267 | 1.276 | 1.265 | 1.304 | 1.278 | 0.016 | -2.04 |
| | 0.000 | 1.305 | 1.265 | 1.277 | 1.266 | 1.275 | 1.266 | 1.277 | 1.265 | 1.305 | 1.278 | 0.016 | -2.05 |
| | 0.257 | 1.304 | 1.265 | 1.276 | 1.267 | 1.275 | 1.267 | 1.277 | 1.265 | 1.305 | 1.278 | 0.016 | -2.04 |
| | 0.514 | 1.304 | 1.265 | 1.276 | 1.267 | 1.275 | 1.267 | 1.277 | 1.265 | 1.306 | 1.278 | 0.016 | -2.04 |
| cis-$NH_2$,OH | -0.514 | 1.319 | 1.260 | 1.282 | 1.265 | 1.278 | 1.266 | 1.280 | 1.262 | 1.314 | 1.280 | 0.022 | -1.96 |
| | -0.257 | 1.320 | 1.259 | 1.282 | 1.265 | 1.278 | 1.266 | 1.280 | 1.262 | 1.313 | 1.280 | 0.022 | -1.96 |
| | 0.000 | 1.321 | 1.258 | 1.283 | 1.264 | 1.278 | 1.266 | 1.280 | 1.263 | 1.313 | 1.281 | 0.022 | -1.95 |
| | 0.257 | 1.322 | 1.257 | 1.283 | 1.264 | 1.278 | 1.266 | 1.279 | 1.263 | 1.312 | 1.281 | 0.023 | -1.95 |
| | 0.514 | 1.324 | 1.256 | 1.284 | 1.263 | 1.279 | 1.266 | 1.280 | 1.264 | 1.312 | 1.281 | 0.023 | -1.95 |
| cis-$NO_2$,CN | -0.514 | 1.308 | 1.258 | 1.278 | 1.263 | 1.276 | 1.263 | 1.278 | 1.258 | 1.314 | 1.277 | 0.021 | -2.11 |
| | -0.257 | 1.307 | 1.258 | 1.278 | 1.263 | 1.276 | 1.263 | 1.278 | 1.258 | 1.314 | 1.277 | 0.021 | -2.11 |
| | 0.000 | 1.307 | 1.259 | 1.278 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.315 | 1.277 | 0.021 | -2.11 |
| | 0.257 | 1.306 | 1.259 | 1.277 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.315 | 1.277 | 0.021 | -2.11 |
| | 0.514 | 1.306 | 1.259 | 1.277 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.316 | 1.277 | 0.021 | -2.11 |
| cis-$NO_2$,$NH_2$ | -0.514 | 1.317 | 1.252 | 1.288 | 1.255 | 1.287 | 1.254 | 1.292 | 1.247 | 1.332 | 1.280 | 0.031 | -2.06 |
| | -0.257 | 1.315 | 1.253 | 1.286 | 1.256 | 1.286 | 1.255 | 1.291 | 1.249 | 1.330 | 1.280 | 0.029 | -2.06 |
| | 0.000 | 1.314 | 1.254 | 1.285 | 1.257 | 1.284 | 1.256 | 1.289 | 1.250 | 1.329 | 1.280 | 0.028 | -2.06 |
| | 0.257 | 1.313 | 1.255 | 1.284 | 1.258 | 1.283 | 1.257 | 1.288 | 1.251 | 1.327 | 1.280 | 0.027 | -2.06 |
| | 0.514 | 1.311 | 1.256 | 1.282 | 1.259 | 1.282 | 1.258 | 1.287 | 1.252 | 1.326 | 1.279 | 0.026 | -2.06 |
| cis-$NO_2$,OH | -0.514 | 1.313 | 1.255 | 1.283 | 1.259 | 1.281 | 1.259 | 1.284 | 1.255 | 1.319 | 1.279 | 0.024 | -2.07 |
| | -0.257 | 1.312 | 1.256 | 1.282 | 1.260 | 1.280 | 1.260 | 1.283 | 1.256 | 1.318 | 1.279 | 0.024 | -2.07 |
| | 0.000 | 1.311 | 1.256 | 1.281 | 1.261 | 1.279 | 1.261 | 1.282 | 1.257 | 1.317 | 1.278 | 0.023 | -2.08 |
| | 0.257 | 1.310 | 1.257 | 1.280 | 1.261 | 1.278 | 1.261 | 1.281 | 1.258 | 1.316 | 1.278 | 0.022 | -2.08 |
| | 0.514 | 1.309 | 1.257 | 1.279 | 1.262 | 1.278 | 1.262 | 1.281 | 1.259 | 1.315 | 1.278 | 0.021 | -2.08 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| trans-$NH_2$,OH | -0.514 | 1.319 | 1.259 | 1.282 | 1.265 | 1.278 | 1.266 | 1.280 | 1.262 | 1.314 | 1.280 | 0.022 | -1.96 |
| | -0.257 | 1.320 | 1.259 | 1.282 | 1.265 | 1.278 | 1.266 | 1.280 | 1.262 | 1.313 | 1.280 | 0.022 | -1.96 |
| | 0.000 | 1.321 | 1.258 | 1.283 | 1.264 | 1.278 | 1.266 | 1.280 | 1.263 | 1.313 | 1.281 | 0.022 | -1.95 |
| | 0.257 | 1.322 | 1.257 | 1.283 | 1.264 | 1.278 | 1.266 | 1.279 | 1.263 | 1.312 | 1.281 | 0.023 | -1.95 |
| | 0.514 | 1.324 | 1.256 | 1.284 | 1.263 | 1.279 | 1.266 | 1.280 | 1.264 | 1.312 | 1.281 | 0.023 | -1.95 |
| trans-$NO_2$,CN | -0.514 | 1.308 | 1.258 | 1.278 | 1.263 | 1.276 | 1.263 | 1.278 | 1.258 | 1.314 | 1.277 | 0.021 | -2.11 |
| | -0.257 | 1.307 | 1.258 | 1.278 | 1.263 | 1.276 | 1.263 | 1.278 | 1.258 | 1.314 | 1.277 | 0.021 | -2.11 |
| | 0.000 | 1.307 | 1.259 | 1.278 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.315 | 1.277 | 0.021 | -2.11 |
| | 0.257 | 1.306 | 1.259 | 1.277 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.315 | 1.277 | 0.021 | -2.11 |
| | 0.514 | 1.306 | 1.259 | 1.277 | 1.263 | 1.276 | 1.263 | 1.279 | 1.258 | 1.316 | 1.277 | 0.021 | -2.11 |
| trans-$NO_2$,$NH_2$ | -0.514 | 1.317 | 1.252 | 1.288 | 1.255 | 1.287 | 1.254 | 1.292 | 1.247 | 1.332 | 1.280 | 0.031 | -2.06 |
| | -0.257 | 1.315 | 1.253 | 1.286 | 1.256 | 1.286 | 1.255 | 1.291 | 1.249 | 1.330 | 1.280 | 0.029 | -2.06 |
| | 0.000 | 1.314 | 1.254 | 1.285 | 1.257 | 1.284 | 1.256 | 1.289 | 1.250 | 1.329 | 1.280 | 0.028 | -2.06 |
| | 0.257 | 1.313 | 1.255 | 1.284 | 1.258 | 1.283 | 1.257 | 1.288 | 1.251 | 1.327 | 1.280 | 0.027 | -2.06 |
| | 0.514 | 1.311 | 1.256 | 1.282 | 1.259 | 1.282 | 1.258 | 1.287 | 1.252 | 1.326 | 1.279 | 0.026 | -2.06 |
| trans-$NO_2$,OH | -0.514 | 1.313 | 1.255 | 1.283 | 1.259 | 1.281 | 1.259 | 1.284 | 1.255 | 1.319 | 1.279 | 0.024 | -2.07 |
| | -0.257 | 1.312 | 1.256 | 1.282 | 1.260 | 1.280 | 1.260 | 1.283 | 1.256 | 1.318 | 1.279 | 0.023 | -2.07 |
| | 0.000 | 1.311 | 1.256 | 1.281 | 1.261 | 1.279 | 1.261 | 1.282 | 1.257 | 1.317 | 1.278 | 0.023 | -2.08 |
| | 0.257 | 1.310 | 1.257 | 1.280 | 1.261 | 1.278 | 1.262 | 1.281 | 1.258 | 1.316 | 1.278 | 0.022 | -2.08 |
| | 0.514 | 1.309 | 1.257 | 1.279 | 1.262 | 1.278 | 1.262 | 1.281 | 1.259 | 1.315 | 1.278 | 0.021 | -2.08 |
| polyyne | -0.514 | 1.199 | 1.362 | 1.207 | 1.354 | 1.208 | 1.354 | 1.206 | 1.361 | 1.198 | 1.272 | 0.081 | -3.83 |
| | -0.257 | 1.199 | 1.362 | 1.206 | 1.353 | 1.208 | 1.353 | 1.206 | 1.362 | 1.199 | 1.272 | 0.081 | -3.83 |
| | 0.000 | 1.199 | 1.362 | 1.206 | 1.353 | 1.208 | 1.353 | 1.206 | 1.362 | 1.199 | 1.272 | 0.081 | -3.83 |
| | 0.257 | 1.199 | 1.362 | 1.206 | 1.353 | 1.208 | 1.353 | 1.206 | 1.362 | 1.199 | 1.272 | 0.081 | -3.83 |
| | 0.514 | 1.198 | 1.361 | 1.206 | 1.354 | 1.208 | 1.354 | 1.207 | 1.362 | 1.199 | 1.272 | 0.081 | -3.83 |
| py-$NH_2$,OH | -0.514 | 1.204 | 1.357 | 1.209 | 1.353 | 1.210 | 1.353 | 1.208 | 1.359 | 1.199 | 1.273 | 0.079 | -3.71 |
| | -0.257 | 1.205 | 1.356 | 1.210 | 1.352 | 1.210 | 1.353 | 1.208 | 1.359 | 1.199 | 1.273 | 0.079 | -3.71 |
| | 0.000 | 1.205 | 1.355 | 1.210 | 1.352 | 1.210 | 1.353 | 1.208 | 1.360 | 1.199 | 1.273 | 0.079 | -3.70 |
| | 0.257 | 1.206 | 1.355 | 1.210 | 1.352 | 1.210 | 1.353 | 1.208 | 1.360 | 1.199 | 1.273 | 0.078 | -3.70 |
| | 0.514 | 1.206 | 1.354 | 1.210 | 1.352 | 1.210 | 1.353 | 1.208 | 1.361 | 1.199 | 1.273 | 0.078 | -3.69 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| py-$NO_2$,CN | -0.514 | 1.197 | 1.356 | 1.207 | 1.351 | 1.208 | 1.351 | 1.208 | 1.354 | 1.203 | 1.270 | 0.078 | -3.81 |
| | -0.257 | 1.197 | 1.356 | 1.207 | 1.351 | 1.208 | 1.351 | 1.208 | 1.354 | 1.203 | 1.270 | 0.078 | -3.81 |
| | 0.000 | 1.197 | 1.356 | 1.207 | 1.351 | 1.208 | 1.351 | 1.208 | 1.353 | 1.203 | 1.270 | 0.078 | -3.81 |
| | 0.257 | 1.197 | 1.357 | 1.206 | 1.351 | 1.208 | 1.351 | 1.208 | 1.353 | 1.204 | 1.270 | 0.078 | -3.81 |
| | 0.514 | 1.196 | 1.357 | 1.206 | 1.351 | 1.208 | 1.351 | 1.208 | 1.353 | 1.204 | 1.270 | 0.078 | -3.81 |
| py-$NO_2$,$NH_2$ | -0.514 | 1.199 | 1.353 | 1.210 | 1.347 | 1.212 | 1.347 | 1.212 | 1.349 | 1.208 | 1.271 | 0.074 | -3.66 |
| | -0.257 | 1.199 | 1.354 | 1.209 | 1.348 | 1.211 | 1.348 | 1.211 | 1.350 | 1.207 | 1.271 | 0.075 | -3.68 |
| | 0.000 | 1.199 | 1.354 | 1.209 | 1.349 | 1.211 | 1.348 | 1.211 | 1.351 | 1.206 | 1.271 | 0.076 | -3.70 |
| | 0.257 | 1.198 | 1.355 | 1.208 | 1.350 | 1.210 | 1.349 | 1.210 | 1.352 | 1.206 | 1.271 | 0.076 | -3.72 |
| | 0.514 | 1.198 | 1.355 | 1.208 | 1.350 | 1.210 | 1.350 | 1.210 | 1.353 | 1.205 | 1.271 | 0.077 | -3.73 |
| py-$NO_2$,OH | -0.514 | 1.199 | 1.354 | 1.209 | 1.349 | 1.210 | 1.350 | 1.209 | 1.356 | 1.200 | 1.271 | 0.078 | -3.79 |
| | -0.257 | 1.198 | 1.355 | 1.208 | 1.350 | 1.210 | 1.351 | 1.208 | 1.357 | 1.200 | 1.271 | 0.078 | -3.80 |
| | 0.000 | 1.198 | 1.355 | 1.208 | 1.350 | 1.209 | 1.351 | 1.208 | 1.357 | 1.199 | 1.271 | 0.079 | -3.81 |
| | 0.257 | 1.198 | 1.356 | 1.207 | 1.351 | 1.209 | 1.352 | 1.208 | 1.358 | 1.199 | 1.271 | 0.079 | -3.82 |
| | 0.514 | 1.197 | 1.356 | 1.207 | 1.351 | 1.209 | 1.352 | 1.207 | 1.358 | 1.199 | 1.271 | 0.079 | -3.83 |

**Table S6** Elements of polarizability tensor α in $Å^3$ in unsubstituted and substituted cumulenes and polyynes in electric field *F*, computed using CAM-B3LYP/ aug-cc-pVTZ

| | *F* (V/Å) | $\alpha_{xx}$ | $\alpha_{yx}$ | $\alpha_{yy}$ | $\alpha_{zx}$ | $\alpha_{zy}$ | $\alpha_{zz}$ | Tr(α) |
|---|---|---|---|---|---|---|---|---|
| cumulene | -0.514 | 99.754 | 0.000 | 10.263 | 0.000 | 0.000 | 9.881 | 39.966 |
| | -0.257 | 99.731 | 0.000 | 10.261 | 0.000 | 0.000 | 9.878 | 39.957 |
| | 0.000 | 99.739 | 0.000 | 10.260 | 0.000 | 0.000 | 9.877 | 39.959 |
| | 0.257 | 99.731 | 0.000 | 10.261 | 0.000 | 0.000 | 9.878 | 39.957 |
| | 0.514 | 99.754 | 0.000 | 10.263 | 0.000 | 0.000 | 9.881 | 39.966 |
| cis-$NH_2$,OH | -0.514 | 118.466 | 2.922 | 13.090 | 0.133 | 0.021 | 11.140 | 47.565 |
| | -0.257 | 118.617 | 3.052 | 13.095 | 0.065 | 0.016 | 11.132 | 47.615 |
| | 0.000 | 118.803 | 3.182 | 13.099 | -0.015 | 0.009 | 11.126 | 47.676 |
| | 0.257 | 119.013 | 3.311 | 13.103 | -0.116 | -0.003 | 11.122 | 47.746 |
| | 0.514 | 119.258 | 3.445 | 13.105 | -0.256 | -0.023 | 11.120 | 47.828 |
| cis-$NO_2$,CN | -0.514 | 130.254 | -1.939 | 16.223 | 0.000 | 0.001 | 11.653 | 52.710 |
| | -0.257 | 129.973 | -2.091 | 16.177 | 0.000 | 0.001 | 11.655 | 52.602 |
| | 0.000 | 129.744 | -2.242 | 16.132 | -0.001 | 0.001 | 11.658 | 52.511 |
| | 0.257 | 129.580 | -2.390 | 16.087 | 0.000 | 0.001 | 11.661 | 52.443 |
| | 0.514 | 129.471 | -2.534 | 16.038 | -0.001 | 0.001 | 11.665 | 52.392 |
| cis-$NO_2$,$NH_2$ | -0.514 | 136.250 | 2.353 | 15.021 | -0.011 | -0.002 | 11.554 | 54.275 |
| | -0.257 | 135.025 | 2.218 | 15.059 | -0.011 | -0.002 | 11.558 | 53.881 |
| | 0.000 | 133.806 | 2.090 | 15.110 | -0.011 | -0.002 | 11.564 | 53.493 |
| | 0.257 | 132.632 | 1.971 | 15.175 | -0.011 | -0.002 | 11.571 | 53.126 |
| | 0.514 | 131.492 | 1.861 | 15.253 | -0.011 | -0.002 | 11.580 | 52.775 |
| cis-$NO_2$,OH | -0.514 | 123.871 | 2.675 | 14.343 | 0.000 | 0.000 | 11.026 | 49.747 |
| | -0.257 | 123.016 | 2.522 | 14.359 | 0.003 | 0.000 | 11.025 | 49.467 |
| | 0.000 | 122.151 | 2.373 | 14.384 | 0.002 | 0.000 | 11.025 | 49.187 |
| | 0.257 | 121.376 | 2.234 | 14.414 | 0.000 | 0.000 | 11.027 | 48.939 |
| | 0.514 | 120.640 | 2.102 | 14.452 | 0.000 | 0.000 | 11.029 | 48.707 |
| trans-$NH_2$,OH | -0.514 | 118.218 | 7.617 | 13.439 | 0.073 | 0.020 | 11.141 | 47.599 |
| | -0.257 | 118.381 | 7.685 | 13.442 | 0.009 | 0.013 | 11.133 | 47.652 |
| | 0.000 | 118.568 | 7.753 | 13.446 | -0.063 | 0.004 | 11.127 | 47.714 |
| | 0.257 | 118.772 | 7.818 | 13.452 | -0.154 | -0.010 | 11.123 | 47.782 |
| | 0.514 | 119.009 | 7.888 | 13.459 | -0.287 | -0.033 | 11.121 | 47.863 |
| trans-$NO_2$,CN | -0.514 | 129.857 | 11.031 | 16.946 | 0.000 | 0.000 | 11.649 | 52.817 |
| | -0.257 | 129.728 | 10.883 | 16.800 | -0.001 | 0.000 | 11.651 | 52.726 |
| | 0.000 | 129.599 | 10.727 | 16.671 | -0.001 | 0.000 | 11.654 | 52.641 |
| | 0.257 | 129.476 | 10.569 | 16.560 | -0.001 | 0.000 | 11.657 | 52.564 |
| | 0.514 | 129.358 | 10.411 | 16.469 | -0.001 | 0.000 | 11.661 | 52.496 |
| trans-$NO_2$,$NH_2$ | -0.514 | 135.736 | 10.587 | 15.728 | -0.011 | -0.001 | 11.554 | 54.339 |
| | -0.257 | 134.694 | 10.256 | 15.660 | -0.011 | -0.001 | 11.559 | 53.971 |
| | 0.000 | 133.712 | 9.942 | 15.599 | -0.011 | -0.001 | 11.565 | 53.625 |
| | 0.257 | 132.784 | 9.644 | 15.545 | -0.011 | -0.001 | 11.572 | 53.300 |
| | 0.514 | 131.913 | 9.359 | 15.499 | -0.011 | -0.001 | 11.581 | 52.997 |
| trans-$NO_2$,OH | -0.514 | 123.537 | 7.932 | 14.750 | 0.000 | 0.000 | 11.024 | 49.771 |
| | -0.257 | 122.778 | 7.678 | 14.705 | -0.001 | 0.000 | 11.024 | 49.502 |
| | 0.000 | 122.081 | 7.438 | 14.666 | 0.000 | 0.000 | 11.024 | 49.257 |
| | 0.257 | 121.422 | 7.209 | 14.634 | -0.002 | 0.000 | 11.025 | 49.027 |
| | 0.514 | 120.828 | 6.988 | 14.607 | 0.000 | 0.000 | 11.027 | 48.821 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| polyyne | -0.514 | 62.042 | 0.000 | 9.318 | 0.000 | 0.000 | 9.318 | 26.893 |
| | -0.257 | 62.000 | 0.000 | 9.316 | 0.000 | 0.000 | 9.316 | 26.877 |
| | 0.000 | 61.986 | 0.000 | 9.316 | 0.000 | 0.000 | 9.316 | 26.873 |
| | 0.257 | 62.000 | 0.000 | 9.316 | 0.000 | 0.000 | 9.316 | 26.877 |
| | 0.514 | 62.042 | 0.000 | 9.318 | 0.000 | 0.000 | 9.318 | 26.893 |
| py-$NH_2$,OH | -0.514 | 74.816 | 0.176 | 10.706 | 0.015 | 0.000 | 10.664 | 32.062 |
| | -0.257 | 74.874 | 0.154 | 10.703 | 0.016 | -0.001 | 10.662 | 32.079 |
| | 0.000 | 74.993 | 0.143 | 10.703 | 0.014 | -0.001 | 10.660 | 32.118 |
| | 0.257 | 75.177 | 0.132 | 10.706 | 0.014 | -0.001 | 10.658 | 32.180 |
| | 0.514 | 75.415 | 0.119 | 10.712 | 0.015 | -0.001 | 10.657 | 32.261 |
| py-$NO_2$,CN | -0.514 | 93.427 | -0.001 | 13.401 | 0.000 | -0.077 | 11.225 | 39.351 |
| | -0.257 | 93.024 | -0.001 | 13.403 | 0.000 | -0.077 | 11.227 | 39.218 |
| | 0.000 | 92.741 | -0.002 | 13.405 | 0.000 | -0.077 | 11.229 | 39.125 |
| | 0.257 | 92.573 | -0.001 | 13.408 | 0.000 | -0.077 | 11.231 | 39.071 |
| | 0.514 | 92.521 | -0.001 | 13.411 | 0.000 | -0.077 | 11.233 | 39.055 |
| py-$NO_2$,$NH_2$ | -0.514 | 92.755 | 0.001 | 13.382 | -0.531 | -0.003 | 11.112 | 39.083 |
| | -0.257 | 90.972 | 0.002 | 13.385 | -0.443 | -0.004 | 11.116 | 38.491 |
| | 0.000 | 89.415 | 0.002 | 13.388 | -0.379 | -0.004 | 11.122 | 37.975 |
| | 0.257 | 88.058 | 0.003 | 13.392 | -0.326 | -0.004 | 11.128 | 37.526 |
| | 0.514 | 86.862 | 0.002 | 13.397 | -0.273 | -0.004 | 11.134 | 37.131 |
| py-$NO_2$,OH | -0.514 | 83.066 | 0.644 | 12.890 | -0.230 | -0.002 | 10.590 | 35.515 |
| | -0.257 | 82.007 | 0.627 | 12.894 | -0.226 | -0.002 | 10.591 | 35.164 |
| | 0.000 | 81.063 | 0.612 | 12.900 | -0.223 | -0.002 | 10.592 | 34.852 |
| | 0.257 | 80.226 | 0.598 | 12.907 | -0.220 | -0.002 | 10.593 | 34.576 |
| | 0.514 | 79.488 | 0.586 | 12.917 | -0.217 | -0.001 | 10.595 | 34.333 |

**Table S7** HOMO-LUMO gap energies (in eV) in unsubstituted and substituted cumulenes and polyynes in electric field *F*, computed using CAM-B3LYP/ aug-cc-pVTZ

| | | cis-cumulenes | | | | trans-cumulenes | | | | polyynes | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *F* (V/Å) | cumu-lene | cis-$NH_2$,OH | cis-$NO_2$,CN | cis-$NO_2$,$NH_2$ | cis-$NO_2$,OH | trans-$NH_2$,OH | trans-$NO_2$,CN | trans-$NO_2$,$NH_2$ | trans-$NO_2$,OH | polyyne | py-$NH_2$,OH | py-$NO_2$,CN | py-$NO_2$,$NH_2$ | py-$NO_2$,OH |
| -0.514 | 4.86 | 4.53 | 4.46 | 4.20 | 4.41 | 4.53 | 4.46 | 4.20 | 4.41 | 6.54 | 6.24 | 5.69 | 5.06 | 5.45 |
| -0.257 | 4.86 | 4.52 | 4.47 | 4.23 | 4.43 | 4.52 | 4.47 | 4.23 | 4.44 | 6.54 | 6.22 | 5.75 | 5.18 | 5.55 |
| 0 | 4.86 | 4.52 | 4.48 | 4.26 | 4.46 | 4.52 | 4.48 | 4.26 | 4.46 | 6.55 | 6.19 | 5.80 | 5.30 | 5.65 |
| 0.257 | 4.86 | 4.51 | 4.49 | 4.28 | 4.49 | 4.51 | 4.49 | 4.28 | 4.49 | 6.54 | 6.16 | 5.83 | 5.42 | 5.75 |
| 0.514 | 4.86 | 4.50 | 4.49 | 4.31 | 4.51 | 4.50 | 4.49 | 4.31 | 4.51 | 6.54 | 6.13 | 5.86 | 5.54 | 5.84 |