## Supplementary Information for:

# Quantum Chemical Investigation of Epoxide and Ether Groups in Graphene Oxide and their Vibrational Spectra

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**Table S1.** Degree of  $\pi$ -conjugation in oxidized graphene flakes computed using the topological invariants, the number of Kekulé structures and the number of Clar covers. The entries are given relative to the analogous invariants of pristine structures. Page S20.

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#### 1. Comparison of DFT and DFTB IR Spectra for Species 1.

DFT and DFTB IR spectra of all isomers of **10** between 600 - 1800 cm<sup>-1</sup> are given in Fig. S7. As anticipated, DFT and DFTB vibrational eigenvalues are in very good agreement with each other (Fig. S7(c)). Comparison of Fig. S7(a) and (b) also show that the corresponding peak intensities are also in qualitative agreement. All **10** isomers exhibit a vibrational band at ca. 800 cm<sup>-1</sup>, which corresponds to the C-H breathing vibrational mode. For many of the  $\alpha$ - $\eta$  10 isomers, this is the most intense band of the vibrational spectrum in this region. However, for the  $\alpha$  and  $\gamma$  isomers, which correspond to ether species, this is not the case. In the case of the former isomer, the IR spectrum consists of three distinct bands between  $600 - 1800 \text{ cm}^{-1}$ . Near 800 cm<sup>-1</sup>, in addition to the C-H breathing mode mentioned above, the C-O-C bending/breathing mode is also observed. The symmetric and asymmetric stretches of the C-O-C group correspond to the intense peaks between 1200 and 1300 cm<sup>-1</sup>. The coupling of these C-O-C modes with the 'wagging' of the C-H bonds results in the vibrational band at *ca*. 1500 cm<sup>-1</sup>. With respect to the  $\gamma$  **10** isomer, while the band structure near 800 cm<sup>-1</sup> remains, the IR spectral structure of the  $\alpha$  isomer is lost between 1000 – 1800 cm<sup>-1</sup>. In its place is a more consistently spaced group of IR peaks. However, these peaks are associated with vibrational modes of similar nature in both cases. Between 1000 and 1500 cm<sup>-1</sup> the C-O-C asymmetric stretch couples with the C-H 'wagging', with the former being dominant near 1000 cm<sup>-1</sup>, and the latter being dominant near 1500 cm<sup>-1</sup>. It is noted also that the  $\gamma$  10 isomer exhibits a lone peak at ca. 1700 cm<sup>-1</sup>, which is unobserved for all other 10 isomers. This peak corresponds to a coupled C-O-C and C-C stretching mode. These differences between  $\alpha$  and  $\gamma$  **10** IR spectra are attributed to the alignment of the dipole derivative vectors with respect to the equilibrium geometry of respective isomers. This difference also explains the lack of spectral features of the other 10 isomers in this region. In these cases, the respective C-C bond remains intact at the equilibrium geometry, which results in a marked decrease in the magnitude of the dipole moment. From comparison of Fig. 2(a) and Fig. S7 therefore, it is evident that there is a distinct correlation in the IR spectral features of 10 isomers, and their relative energetics. Most notably, those isomers for which structural deformation results in C-C bond cleavage and the formation of a genuine ether functional group possess distinct IR spectral signatures between 1000 and 1800 cm<sup>-1</sup> (a, g). It is noted also that this conclusion holds for both the DFT and DFTB computed IR spectra of these species.



Figure S1. Comparison of 250 DFT and DFTB optimized bond lengths of phenanthrene 1 and 10 isomers with different oxygen position. Red lines are the result of linear regression analysis, which yielded a slope of 1.02, and an  $R^2$  value of 0.986.



Figure S2.  $\Delta E$ (SDFTB) for singlet-state 20 – 50 and 70 – 110 as a function of oxygen position. Oxygen positions are defined in Fig. 1 in the main text. Asterisks denote positions at which oxidation leads to the formation of an ether functional group.



**Figure S3.**  $\Delta E$ (SDFTB) for triplet-state **20** – **50** and **70** – **110** as a function of oxygen position. Oxygen positions are defined in Fig. 1 in the main text.



**Figure S4.**  $\Delta E$  (red),  $E_{int}$  (green) and  $E_{def}$  (blue) for oxygen at positions analogous to the (a)  $\gamma$  and (b)  $\phi$  of **10**, for species **9**. The effects of conjugation disruption and structural deformation on the total DFTB energy are qualitatively equivalent to that observed for the model **10** system (Fig. 2). Energy contours are spaced at intervals of 10 kJmol<sup>-1</sup>. In each case, *R* denotes the C-C bond length of the C-O-C functional group; atoms C<sub>1</sub> – C<sub>4</sub> are defined in the figure.

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**Figure S5.** Correlation between topological aromaticity and DFTB energies for un-optimized (sp) and optimized (opt) oxidized HGF structures. Aromaticity is given in % relative to the pristine HGF.



Figure S5 cont'd

![](_page_9_Figure_1.jpeg)

Figure S5 cont'd

![](_page_10_Figure_1.jpeg)

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Figure S5 cont'd

![](_page_18_Figure_1.jpeg)

**Figure S6.** IR spectra of phenanthrene **1** and **10** as a function of oxygen position calculated using (a) DFT and (b) DFTB. Spectra are ordered and colored according to the relative DFTB energy of the respective isomer (blue = lowest energy, red = highest energy). Isomer labels  $\alpha$ - $\eta$  are defined in Fig. 1(a). (c) Comparison of 690 **10** vibrational eigenvalues for  $\alpha$ - $\eta$  isomers computed using DFT and DFTB. Linear regression, resulting in the red line, yields a coefficient of 0.941 and an  $R^2$  value of 0.999.

**Table S1.** Degree of  $\pi$ -conjugation in oxidized graphene flakes computed using the topological invariants, the number of Kekulé structures and the number of Clar covers. The entries are given relative to the analogous invariants of pristine structures.

| 1 014110 |             |                   |
|----------|-------------|-------------------|
| Position | Clar covers | Kekulé structures |
| α        | 9.09%       | 20.00%            |
| β        | 27.27%      | 40.00%            |
| χ        | 45.45%      | 60.00%            |
| $\delta$ | 27.27%      | 40.00%            |
| З        | 45.45%      | 60.00%            |
| arphi    | 27.27%      | 40.00%            |
| l        | 27.27%      | 40.00%            |
| γ        | 9.09%       | 20.00%            |
| η        | 81.82%      | 80.00%            |

| 1 | C.H.         |  |
|---|--------------|--|
| L | $C_{141110}$ |  |

#### $2 C_{42}H_{18}$

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 32.11%      | 40.00%            |
| 2        | 7.14%       | 20.00%            |
| 3        | 28.58%      | 40.00%            |
| 4        | 3.57%       | 10.00%            |
| 5        | 35.71%      | 50.00%            |
| 6        | 35.71%      | 50.00%            |

**3** C<sub>114</sub>H<sub>30</sub>

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 30.30%      | 37.49%            |
| 2        | 11.62%      | 25.02%            |
| 3        | 29.49%      | 37.49%            |
| 4        | 10.31%      | 22.94%            |
| 5        | 31.69%      | 39.57%            |
| 6        | 31.95%      | 38.27%            |
| 7        | 9.02%       | 22.16%            |
| 8        | 25.36%      | 35.22%            |
| 9        | 9.04%       | 23.47%            |
| 10       | 31.62%      | 42.62%            |
| 11       | 27.49%      | 38.27%            |

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| 12 | 4.52%  | 11.73% |
|----|--------|--------|
| 13 | 34.39% | 45.65% |
| 14 | 40.39% | 54.35% |
| 15 | 36.26% | 50.00% |
| 17 | 36.26% | 50.00% |

## ${\bf 4} \quad C_{222}H_{42}$

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 29.17%      | 36.32%            |
| 2        | 14.16%      | 27.35%            |
| 3        | 28.90%      | 36.32%            |
| 4        | 13.60%      | 26.58%            |
| 5        | 29.75%      | 37.09%            |
| 6        | 29.84%      | 36.52%            |
| 7        | 13.07%      | 26.39%            |
| 8        | 27.77%      | 35.43%            |
| 9        | 13.11%      | 26.96%            |
| 10       | 30.24%      | 38.19%            |
| 11       | 28.64%      | 36.52%            |
| 12       | 11.11%      | 23.63%            |
| 13       | 31.04%      | 38.18%            |
| 14       | 31.75%      | 37.44%            |
| 15       | 31.84%      | 39.85%            |
| 16       | 10.37%      | 24.38%            |
| 17       | 31.82%      | 37.81%            |
| 18       | 9.36%       | 22.34%            |
| 19       | 24.70%      | 34.45%            |
| 20       | 30.70%      | 41.16%            |
| 21       | 5.82%       | 14.23%            |
| 22       | 9.61%       | 24.38%            |
| 23       | 32.37%      | 43.20%            |
| 24       | 33.91%      | 44.60%            |
| 25       | 27.19%      | 37.81%            |
| 26       | 4.81%       | 12.19%            |
| 27       | 33.91%      | 44.60%            |
| 28       | 41.59%      | 55.40%            |
| 29       | 36.41%      | 50.00%            |
| 30       | 36.41%      | 50.00%            |

| 5 C1501130 |             |                   |
|------------|-------------|-------------------|
| Position   | Clar covers | Kekulé structures |
| 1          | 27.63%      | 35.43%            |
| 2          | 17.12%      | 29.14%            |
| 3          | 27.49%      | 35.43%            |
| 4          | 18.44%      | 31.06%            |
| 5          | 25.82%      | 33.51%            |
| 6          | 30.50%      | 38.34%            |
| 7          | 16.38%      | 28.15%            |
| 8          | 35.52%      | 42.72%            |
| 9          | 13.00%      | 23.31%            |
| 10         | 21.03%      | 29.14%            |
| 11         | 30.20%      | 38.34%            |
| 12         | 21.57%      | 35.43%            |
| 13         | 28.70%      | 35.43%            |
| 14         | 36.30%      | 47.09%            |
| 15         | 18.71%      | 26.22%            |
| 16         | 10.32%      | 17.48%            |
| 17         | 43.06%      | 50.00%            |
| 18         | 15.08%      | 23.78%            |
| 19         | 75.65%      | 76.22%            |
| 20         | 2.41%       | 6.29%             |
| 21         | 95.24%      | 93.71%            |

## **5** C<sub>150</sub>H<sub>30</sub>

# **6** C<sub>24</sub>H<sub>12</sub>

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| α        | 17.39%      | 30.00%            |
| eta      | 30.43%      | 40.00%            |
| $\delta$ | 65.22%      | 70.00%            |
| χ        | 18.84%      | 30.00%            |

## $7 C_{96}H_{24}$

| Position Clar covers Kekulé structu |
|-------------------------------------|
|-------------------------------------|

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| 1  | 20.36% | 31.39% |
|----|--------|--------|
| 2  | 30.72% | 37.23% |
| 3  | 20.58% | 31.39% |
| 4  | 35.72% | 41.77% |
| 5  | 16.54% | 26.84% |
| 6  | 23.16% | 34.85% |
| 7  | 31.55% | 38.31% |
| 8  | 23.67% | 37.45% |
| 9  | 22.39% | 30.30% |
| 10 | 16.09% | 24.24% |
| 11 | 25.48% | 34.85% |
| 12 | 61.19% | 65.15% |
| 13 | 4.82%  | 10.61% |
| 14 | 90.62% | 89.39% |

## 8 C<sub>216</sub>H<sub>36</sub>

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 21.34%      | 31.96%            |
| 2        | 29.62%      | 36.08%            |
| 3        | 21.41%      | 31.96%            |
| 4        | 31.53%      | 37.89%            |
| 5        | 19.73%      | 30.15%            |
| 6        | 22.58%      | 33.44%            |
| 7        | 29.95%      | 36.40%            |
| 8        | 23.13%      | 34.65%            |
| 9        | 26.46%      | 33.11%            |
| 10       | 19.44%      | 28.95%            |
| 11       | 22.95%      | 33.44%            |
| 12       | 37.21%      | 43.16%            |
| 13       | 17.30%      | 27.89%            |
| 14       | 31.67%      | 41.84%            |
| 15       | 14.28%      | 23.40%            |
| 16       | 23.55%      | 30.27%            |
| 17       | 26.37%      | 37.33%            |
| 18       | 33.12%      | 39.27%            |
| 19       | 25.52%      | 39.35%            |
| 20       | 23.07%      | 30.39%            |
| 21       | 50.77%      | 57.39%            |
| 22       | 18.28%      | 25.34%            |

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| 23 | 14.26% | 21.38% |
|----|--------|--------|
| 24 | 6.31%  | 12.22% |
| 25 | 28.91% | 37.33% |
| 26 | 59.14% | 62.67% |
| 27 | 8.70%  | 15.95% |
| 28 | 85.35% | 84.05% |
| 29 | 1.20%  | 3.73%  |
| 30 | 97.61% | 96.27% |

# 9 C<sub>84</sub>H<sub>24</sub>

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 18.74%      | 30.19%            |
| 2        | 33.39%      | 39.63%            |
| 3        | 19.18%      | 30.19%            |
| 4        | 38.86%      | 43.98%            |
| 5        | 15.07%      | 25.84%            |
| 6        | 18.22%      | 30.87%            |
| 7        | 35.80%      | 43.29%            |
| 8        | 16.49%      | 25.84%            |
| 9        | 27.27%      | 38.26%            |
| 10       | 19.64%      | 30.87%            |
| 11       | 19.64%      | 30.87%            |
| 12       | 63.63%      | 69.13%            |
|          |             |                   |

10 C<sub>180</sub>H<sub>36</sub>

| Position | Clar covers | Kekulé structures |
|----------|-------------|-------------------|
| 1        | 19.66%      | 30.79%            |
| 2        | 32.70%      | 38.43%            |
| 3        | 19.84%      | 30.79%            |
| 4        | 34.44%      | 39.77%            |
| 5        | 18.32%      | 29.44%            |
| 6        | 19.55%      | 30.98%            |
| 7        | 33.73%      | 39.57%            |
| 8        | 19.59%      | 30.76%            |
| 9        | 31.29%      | 38.03%            |
| 10       | 19.22%      | 29.67%            |

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| <br>11 | 20.18% | 30.98% |
|--------|--------|--------|
| 12     | 39.98% | 44.07% |
| 13     | 14.53% | 26.26% |
| 14     | 20.73% | 32.53% |
| 15     | 13.89% | 24.95% |
| 16     | 31.95% | 41.21% |
| 17     | 18.46% | 31.10% |
| 18     | 37.49% | 43.95% |
| 19     | 15.29% | 24.95% |
| 20     | 23.09% | 33.85% |
| 21     | 57.62% | 66.15% |
| 22     | 26.32% | 37.80% |
| 23     | 19.85% | 31.10% |
| 25     | 19.85% | 31.10% |
| 26     | 63.16% | 68.90% |
|        |        |        |

#### 11 C<sub>312</sub>H<sub>48</sub>

| Position | Kekule structures |
|----------|-------------------|
| 1        | 31.25%            |
| 2        | 37.50%            |
| 3        | 31.25%            |
| 4        | 38.06%            |
| 5        | 30.69%            |
| 6        | 31.33%            |
| 7        | 37.99%            |
| 8        | 31.44%            |
| 9        | 37.35%            |
| 10       | 30.57%            |
| 11       | 31.33%            |
| 12       | 39.76%            |
| 13       | 29.67%            |
| 14       | 32.11%            |
| 15       | 28.91%            |
| 16       | 38.22%            |
| 17       | 31.31%            |
| 18       | 39.78%            |
| 19       | 30.74%            |
| 20       | 31.04%            |

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| 21 | 43.60% |
|----|--------|
| 22 | 37.38% |
| 23 | 29.49% |
| 24 | 25.35% |
| 25 | 31.31% |
| 26 | 44.02% |
| 27 | 26.49% |
| 28 | 32.80% |
| 29 | 41.85% |
| 30 | 23.53% |
| 31 | 24.67% |
| 32 | 40.71% |
| 33 | 34.62% |
| 34 | 31.18% |
| 35 | 44.15% |
| 36 | 24.67% |
| 37 | 34.62% |
| 38 | 65.38% |
| 39 | 37.64% |
| 40 | 31.18% |
| 41 | 31.18% |
| 42 | 68.82% |