**Third-Order Electric Field Response of Infinite Linear Chains Composed of Phenalenyl Radicals**

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# Third-Order Electric Field Response of Infinite Linear Chains Composed of Phenalenyl Radicals

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**Abstract**

Open shell singlet di– and multi–radicals are of great importance in the framework of developing organic materials with enhanced nonlinear optical properties. We present here Hartree-Fock and DFT calculations of the structure and static second hyperpolarizabilty ($\gamma$) of the infinite periodic polymer containing stacked planar phenalenyl radicals. At the equilibrium geometry the oligomer structures are closed shell singlets with a significant alternation of the monomer-monomer distances in the stacking direction, thereby forming dimer units. However, the open shell singlet with reduced alternation becomes more favorable at chain lengths greater than about 40 dimer units. In the infinite polymer limit the alternation of stacking distance is essentially zero and the open shell singlet has intermediate diradical character, which is conducive to producing a high value of $\gamma$. DFT functionals, such as B3LYP and PBE0, largely overestimate the value of this property. However, a good estimate for the polymer $\gamma = 1.0 \pm 0.3 \ 10^6$ a.u. per dimer is obtained by a hybrid approach wherein CCSD calculations for the dimer are combined with HF and LC-BLYP results for the polymer/dimer ratio. This value of $\gamma$ is comparable to that found for the -(CH=CH)- unit of polyacetylene. An infinite polymer of stacked coronene molecules was also investigated, showing a considerably smaller enhancement of $\gamma$ with respect to the corresponding dimer.

# 1 Introduction

Since the early 1960s[1–3] there has been a high level of interest in nonlinear optical (NLO) properties from both a theoretical and a practical point of view. In particular, third-order NLO properties, which are governed on the microscopic level by second hyperpolarizabilities, give rise to a diverse set of phenomena including (among others) the electro-optical Kerr effect, electric field induced second harmonic generation, the intensity-dependent refractive

index and third harmonic generation. These phenomena, in turn, have been utilized in a wide variety of applications such as optical memory, holography, optical computing, non-linear microscopy and laser-induced nuclear fusion. In practice, both inorganic and organic NLO materials have been employed, with the former being the more common of the two. However, the development of organic NLO materials is on the ascendancy since they can readily be modified chemically, can often be made cheaply, and high efficiencies are potentially realizable. In addition, systems with widely different desired chemical properties can be realized.

A key consideration is the strength of the system response to the incident radiation. Thus, a great deal of effort has gone into the investigation of structure/function relationships that can serve as a guide to maximizing the hyperpolarizability. Recently, Nakano,[4] Champagne and co-workers have focused on a class of molecules that appear quite promising in the latter respect, namely open shell singlets (di- or multi-radicals). In a long series of papers (see, e.g. Refs. 5–8; a more complete set of citations may be found in Ref. 4) they have shown, both analytically and numerically, that the static hyperpolarizability can be dramatically enhanced for structures with a di-radical character intermediate between that of a pure open shell system and a closed shell singlet. Of course, the static hyperpolarizability is not itself an NLO property, but it is indicative of the strength that can be achieved for the various frequency-dependent NLO processes.

Beyond di-radicals, growing attention has been directed towards open shell singlet multi-radicals.[8–10] In that regard, Yoneda, *et al.*[10] have very recently studied the dimer and tetramer of stacked phenalenyl radicals. They determined, first, that the equilibrium ground state of the dimer is an open shell singlet with an anti-type stacking configuration and an intermediate di-radical character at the equilibrium stacking distance. Moreover, the static hyperpolarizability along the stacking direction was calculated, through a finite field numerical procedure, to be a maximum at that distance with a value per monomer about 30 times that of the isolated monomer. Then, assuming the same geometry and no stacking

distance alternation, they computed a static hyperpolarizability for the singlet tetra-radical that turned out to be more than 4 times the corresponding dimer value. The wide experience gathered in the above-cited work provides strong support for the use of unrestricted DFT, particularly with range-separated hybrids like LC-UBLYP, for studying NLO properties of phenalenyl aggregates, which can be a questionable procedure in other circumstances[11] due to the multi-reference character of many open-shell singlet biradicals. From the above observations it is clearly of interest to determine what enhancement might be achieved for a long chain phenalenyl polymer and, by extension, other multi-radical polymers. To that end we have carried out analytical unrestricted DFT (and Hartree-Fock) static hyperpolarizability calculations on the infinite periodic phenalenyl dimer using a beta version of the `CRYSTAL14` computer code.[12] To the best of our knowledge, this type of polymer has not been treated previously and we believe that the `CRYSTAL` code is ideally suited for such an application. The second-order Coupled Perturbed Hartree-Fock/Kohn-Sham (CPHF/CPKS) methodology that we employ is described in Refs. 13–15. For this paper the code has been extended also to handle gradient-generalized (GGA) functionals for open-shell systems.

In the next section we describe the computational details of our investigation, as well as the main features of the systems we studied. In Section 3.1 we present some preliminary calculations on the dimer unit and small oligomers (tetramer, etc.) that dictate, in part, the computational approaches and parameters that follow. It is seen that the oligomers exhibit a dramatic overshoot of the hyperpolarizability with conventional DFT functionals similar to what is found for ordinary closed shell pi-conjugated polymers. Section 3.2 contains a discussion of our results for the infinite polymer from which we extract the infinite polymer to dimer ratio. Fairly close agreement is found between the unrestricted Hartree-Fock and the range separated LC-UBLYP values for this ratio. Then, a best estimate for the infinite polymer is determined by combining with an Unrestricted Coupled Cluster Singles and Doubles (UCCSD) calculation on the dimer. We close in Section 4 with the conclusions as well as prospects for future work.

# 2    Computational Methods

In this paper we utilize a development version of the CRYSTAL14 code[12] wherein the analytical evaluation of DFT (hyper)polarizabilities by means of the CPHF/CPKS method[13–15] is extended to open shell systems. The computational details (thresholds) of the calculations are reported in detail in the supplementary information. In addition, the GAUSSIAN[29] code has been used for additional finite field UCCSD calculations on the phenalenyl dimer, that are reported in Section 3.2. We tested HF and three different DFT functionals: two global hybrids, B3LYP[16,17] and PBE0,[18] and a long-range corrected one, LC-BLYP.[19]   For the latter, a range separation parameter $\mu = 0.33$ bohr$^{-1}$ has been adopted, which was shown to semi–quantitatively reproduce UCCSD(T) results for hydrocarbon open-shell singlet systems.[20] Global hybrids, as expected,[21] strongly overestimate optical response and the results obtained with these functionals are reported mostly as supplementary information.

There are three different iterative self-consistent steps in the overall procedure. The first of these occurs in calculating the field-free periodic orbitals, which are used to obtain the field-free energy and, thereby, the optimum geometry. In that step the convergence threshold for the field-free energy was taken to be $10^{-8}$ Hartree, while standard default convergence parameters[22] were used for the geometry optimization, in which the semiempirical London-type correction proposed by Grimme[23] has been used. In the subsequent CPHF/CPKS treatment the linear polarizability, $\alpha$, is determined by the first-order wavefunction (or density) obtained through the self-consistent-coupled-perturbed SC-CP1 process. In addition, the second derivative of the wavefunction with respect to the field, computed by the SC-CP2 process, is necessary to determine the second hyperpolarizability, $\gamma$. After a couple of calculations with default values,[22] the convergence criteria for the SC-CP1 and SC-CP2 solutions were set so as to determine both $\alpha$ and $\gamma$ to at least five significant figures.
The $D_{3h}$ phenalenyl radical (see Figure 1) with 13 C atoms, 9 H atoms, and 87 electrons is a polycyclic aromatic hydrocarbon containing 3 six-membered rings. In our periodic cal-

culations the repeat unit is a dimer with the molecular planes orthogonal to the stacking direction and parallel to one another, as shown in Figure 1.
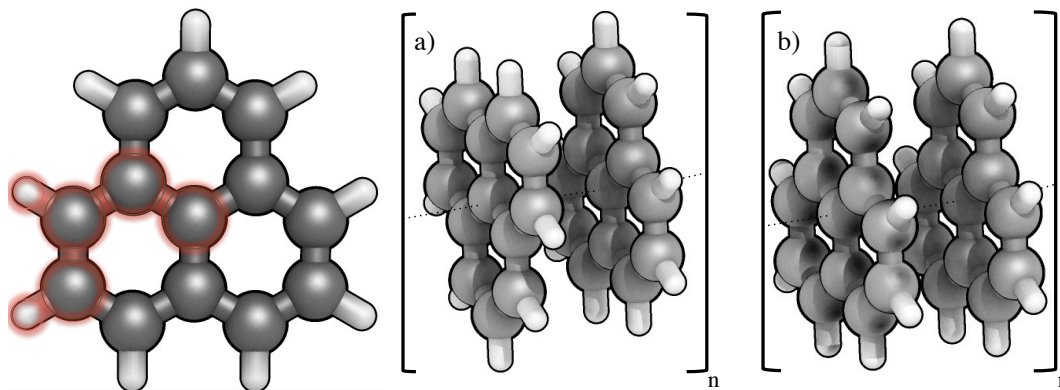


Figure 1: Doublet phenalenyl radical, with symmetry irreducible atoms highlighted, and open shell singlet dimer unit cells in the (a) anti- and (b) eclipsed-type configuration. The molecular planes are orthogonal to the periodicity axis.
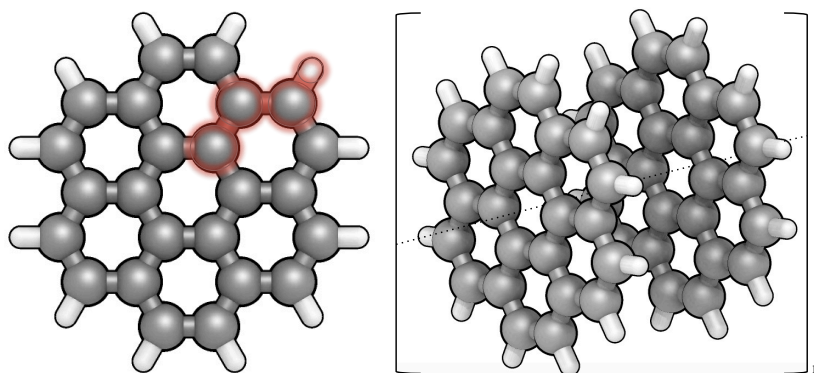


Figure 2: Left panel: coronene molecule, with symmetry irreducible atoms highlighted. Right panel: double unit cell for the infinite polymer of stacked coronene molecules. The molecular planes are orthogonal to the periodicity axis.

The two molecules of the dimer were taken to be in the more stable anti (staggered) configuration in conformity with Yoneda, *et al.*[10] (we did confirm the relative stability of the eclipsed vs. staggered forms). Given the importance of spin, three different spin states were considered, namely, (i) restricted closed shell singlet ($S_c$), (ii) unrestricted open shell singlet ($S_o$) and (iii) unrestricted open shell triplet (T).

In order to compare the results with those of a similar closed-shell system, we have also considered dimers and stacked polymer of coronene (Fig. 2). Evidently, only one mutual orientation between the two molecules is possible in this case.

# 3   Results and Discussion

## 3.1   Dimers and oligomers

Preliminary calculations were carried out on the dimer and small oligomers in order to check out the choice of basis set. For this purpose it is sufficient to use UB3LYP rather than LC-UBLYP, as we have done here for convenience. In general, it is considered important to include diffuse functions in calculating hyperpolarizabilities. Thus, for medium-large systems the 6-31+G* basis[24] is often used as it was by Yoneda, *et al.*[10] For systems extended in one dimension, however, many studies have found that the diffuse functions can be omitted when interested only in the components of the tensor along the periodic direction, as it is the case here. In the following these components, $\alpha_{xx}$ and $\gamma_{xxxx}$ will be simply denoted as $\alpha$ and $\gamma$.

In order to test that possibility we carried out unrestricted open shell singlet UB3LYP-D/6-31G* and UB3LYP-D/6-31+G* (hyper)polarizability calculations for several oligomers using the optimized geometry of an individual planar phenalenyl molecule with a uniform stacking distance of 3.2 Å, which is the reported experimental value for crystalline 2,5,8-tri-tert-butylphenalenyl.[25] Our results are shown in Table 1, where it is seen that for $\mathcal{N}=2$ and, certainly $\mathcal{N}=3$, the two basis sets have already begun to yield very similar values for $\alpha$ and $\gamma$. Thus, all subsequent calculations were carried out using the 6-31G* basis.

The above calculations were done at a representative geometry that is not the same as the (theoretically computed) equilibrium geometry. At this representative geometry the ground state is an open shell singlet in agreement with Yoneda *et al.*[10] Next, we optimized the UB3LYP-D/6-31G* geometry. Although the potential energy surface is quite flat, the

Table 1: Effect of the basis set on the polarizability $\alpha$ and second hyperpolarizability $\gamma$ of phenalenyl oligomers containing 1 to 3 dimers ($\mathcal{N}$) obtained with the UB3LYP functional. Values are reported according to the B-convention.[26] $R_\alpha$ and $R_\gamma$ are the ratio between $\alpha$ and $\gamma$ values obtained with the two basis sets. The stacking distance is the experimental[25] value of 3.2 Å . The molecular geometry has been optimized at the UB3LYP level for the isolated molecule (which is planar) and used as such for all oligomers. 1 a.u. for $\alpha$ is $1.65 \times 10^{-41}$ S.I., while for $\gamma$ is $6.22 \times 10^{-65}$ S.I. .

| | 6-31G* | | 6-31+G* | | $R_\alpha$ | $R_\gamma$ |
|---|---|---|---|---|---|---|
| $\mathcal{N}$ | $\alpha$(a.u.) | $\gamma(\times 10^3)$(a.u.) | $\alpha$(a.u.) | $\gamma(\times 10^3)$(a.u.) | | |
| 1 | 265.8 | $1.216 \times 10^4$ | 320.4 | $2.734 \times 10^4$ | 0.830 | 0.445 |
| 2 | 531.6 | $1.353 \times 10^6$ | 580.2 | $1.418 \times 10^6$ | 0.916 | 0.954 |
| 3 | 838.6 | $7.664 \times 10^6$ | 890.2 | $8.066 \times 10^6$ | 0.942 | 0.950 |

change in properties is striking. The optimization leads to a small degree of non-planarity and, most noteworthy, an alternation of the inter-planar distances (see last row of Table 2) accompanied by a complete loss of open shell character. Indeed, the equilibrium structure becomes identical to what is obtained in a separate restricted closed shell calculation.

An interesting question, then, is what happens in the infinite polymer limit? In fact,

Table 2: Optimized UB3LYP-D/6-31G* distances (in Å) between molecules for a series of phenalenyl oligomers (expressed as number of dimers, $\mathcal{N}$); $d_1^i$ and $d_2^{i,i+1}$ are the inter-planar distances within the $i^{\text{th}}$ dimer and between $i^{\text{th}}$ dimer and its nearest neighbor ($i^{\text{th}} + 1$), respectively, while $\tilde{d}$ is the difference between the last two entries, which corresponds to the alternation of stacking distance at the center of the oligomer. $\infty^R$ and $\infty^U$ refer to the geometries for the infinite polymer optimized using RB3LYP and UB3LYP, respectively.

| $\mathcal{N}$ | $d_1^1$ | $d_2^{12}$ | $d_1^2$ | $d_2^{23}$ | $d_1^3$ | $\tilde{d}$ |
|---|---|---|---|---|---|---|
| 2 | 3.0463 | 3.2085 | - | - | - | 0.1622 |
| 3 | 3.0474 | 3.2032 | 3.0458 | - | - | 0.1574 |
| 4 | 3.0479 | 3.2020 | 3.0465 | 3.1956 | - | 0.1491 |
| 5 | 3.0481 | 3.2019 | 3.0471 | 3.1949 | 3.0480 | 0.1469 |
| $\infty^R$ | 3.0492 | 3.1904 | - | - | - | 0.1412 |
| $\infty^U$ | 3.1110 | 3.1192 | - | - | - | 0.0082 |

a somewhat surprising result will be reported in the following section along with further oligomer calculations done to confirm our finding.

We did not test the robustness of the above geometry optimizations with respect to different functionals, preferring to save that for the polymer calculations, which is our primary con-

cern. Instead, with a view towards the well-known overshoot problem,[27,28] we calculated $\alpha$ and $\gamma$ for different Hamiltonians (see Table 3 and Supplementary Information) at the polymer UB3LYP-D/6-31G* optimized geometry, which produces open shell structures.

UPBE0 and UB3LYP (see SI) definitely exhibit a strong overshoot effect at this geometry.

**Table 3: Values of $\alpha$ and $\gamma$ for oligomers obtained with UHF and LC-UBLYP Hamiltonians at the B3LYP-D/6-31G* optimized geometry of the infinite periodic phenalenyl polymer ($\mathcal{N}$ is the number of dimers in the oligomer). When optimized all oligomers collapse in a closed shell singlet state with molecules that do not show a planar geometry anymore. Note the order of magnitude of the values reported.**

| | UHF | | LC-UBLYP | |
|---|---|---|---|---|
| $\mathcal{N}$ | $\alpha$(a.u.) | $\gamma(\times10)$ (a.u.) | $\alpha$(a.u.) | $\gamma(\times10^3)$ (a.u.) |
| 1 | 102.33 | 259.42 | 147.98 | 136.62 |
| 2 | 124.76 | 754.52 | 205.24 | 419.96 |
| 3 | 134.90 | 1114.7 | 238.18 | 747.42 |
| 4 | 140.77 | 1390.2 | 259.02 | 1036.7 |

The LC-UBLYP results probably overshoot as well, albeit to a much lesser extent. For example, the ratio of the LC-UBLYP $\gamma$ at $\mathcal{N}$=2 vs. the corresponding UHF value is approximately 55, which becomes about 70 at $\mathcal{N}$=4. From our experience both ratios would represent a rather large electron correlation effect (see more later) if that were the only consideration. In the first column of Table 4 we report the values for the second hyperpolarizability $\gamma_{xxxx}$ for the coronene dimer. With the 6-31+G* basis set we reproduced the result obtained by Yoneda *et al.*[10] Thanks to the larger stacking distance with respect to phenalenyl (3.55 Å instead of $\approx$3.0-3.2 Å as in Table 2) we were able to converge calculations for the polymer with an upscaled diffuse exponent (0.08 instead of 0.04), which we note recovers a substantial part of the gap between the 6-31G* and 6-31+G* results.

## 3.2 Infinite Periodic Polymer

As in the case of small oligomers, the anti geometry is favored over eclipsed for the infinite polymer. On the other hand, in contrast with small oligomers, the UB3LYP-D/6-31G* geometry optimization for the polymer leads only to a very slight alternation of the interplanar

Table 4: Second hyperpolarizability $\gamma_{xxxx}$ (in a.u.) per monomer of stacked coronene systems at the LC-UBLYP level, obtained with different basis sets. In the 6-31+(0.08)G* the diffuse exponent of the basis set has been upscaled to 0.08 (from the original 0.04 value).

|  |  | Dimer | Polymer |
| --- | --- | --- | --- |
| LC-UBLYP/6-31G* | $\gamma$ | 390.31 | 1862.82 |
| LC-UBLYP/6-31+(0.08)G* | $\gamma$ | 2807.26 | 10893.76 |
| LC-UBLYP/6-31+G* | $\gamma$ | 5041.81 | – |

spacing (see Table 2) with retention of the open shell singlet character. The reduced alternation of stacking distances is consistent with the behavior of small oligomers of increasing $\mathcal{N}$ as seen in the last column of Table 2, which shows the difference at the center of the oligomer.

Optimization at the RB3LYP-D/6-31G* level, on the other hand, leads to an alternation of stacking distances which is more in line with the trend of oligomers. Fortunately, the properties under study are not dramatically dependent on such geometry changes and, in fact, are only mildly sensitive at the UHF and LC-UBLYP levels (see Table 6), which are the most relevant Hamiltonians in the following discussion.

In order to further verify this surprising behavior we evaluated energy differences between the optimized oligomer in Sec. 2 and the corresponding oligomer obtained at the frozen geometry of the polymer. As shown in Table 5 the relative stability *per dimer* of the optimized oligomers with respect to the "extracted" ones decreases rapidly as the number of dimers increases. Note that, once more, different geometries correspond to different spin states, i.e. with polarized spins (polymer geometry) or unpolarized ("oligomer" geometry), even in the case $\mathcal{N} = \infty$.

The oligomer data is also plotted in Figure 3 where it is seen that a good least squares fit is found for both a linear and a quadratic power series in $1/N$ (with $N$ equal to the number of molecules or twice the number of dimers, $\mathcal{N}$).

Moreover, the constant term in the two series nicely brackets the infinite polymer value. According to the two fits the crossover in stability occurs somewhere between $\mathcal{N}$=36 and

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**Table 5: Energy per dimer, $E^F$, and absolute molecular spin polarization (see text), SP$n$, for phenalenyl oligomers calculated at the "frozen" UB3LYP-D/6-31G\* geometry of the infinite periodic polymer. For comparison the energy at the optimized oligomer geometry, $E^O$, in a closed shell singlet state with null spin polarization is also given along with the energy difference between the two ($\Delta E = E^O - E^F$). The subscript $n$ for the absolute spin polarization increases from the molecule at the end of the chain to the molecule at the center. The spin polarization (SP) value for the infinite polymer is 0.463.**

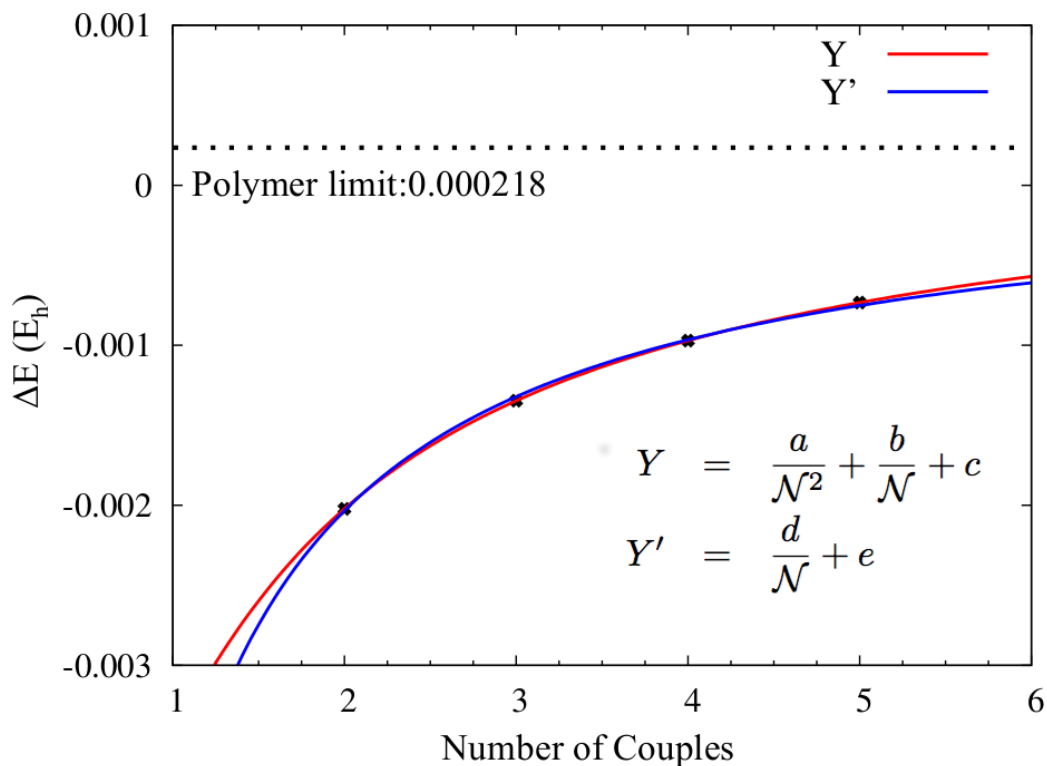| $\mathcal{N}$ | $E^F$ (Ha) | $E^O$ (Ha) | $\Delta E$ (mHa) | SP$_1$ | SP$_2$ | SP$_3$ | SP$_4$ | SP$_5$ |
|---|---|---|---|---|---|---|---|---|
| 2 | -1001.047996 | -1001.050018 | -2.022 | 0.429 | 0.598 | - | - | - |
| 3 | -1001.052387 | -1001.053733 | -1.346 | 0.420 | 0.629 | 0.490 | - | - |
| 4 | -1001.054619 | -1001.055590 | -0.971 | 0.418 | 0.634 | 0.463 | 0.501 | - |
| 5 | -1001.055962 | -1001.056695 | -0.733 | 0.416 | 0.635 | 0.456 | 0.503 | 0.471 |
| $\infty$ | -1001.061310 | -1001.061092 | 0.218 | - | - | - | - | - |



Figure 3: Difference in energy between the geometry extracted from the infinite periodic phenalenyl polymer and the geometry optimized of the phenalenyl oligomer as a function of the number of molecules in the oligomer. Y and Y' are the two fitting functions, whose parameters are: $a = (181.029 \pm 2.589) \times 10^{-5}$, $b = (-556.311 \pm 1.854) \times 10^{-5}$, $c = (30.701 \pm 0.300) \times 10^{-5}$; $d = (-42.747 \pm 1.039) \times 10^{-4}$, $e = (10.347 \pm 3.536) \times 10^{-5}$.

$\mathcal{N}$=42 dimers.

It is also of interest to consider the evolution of the absolute spin polarization on each monomer, at the extracted geometry, as reported in Table 5. This property was calculated as the sum of the residual atomic spin density on each atom belonging to the molecule. For each $\mathcal{N}$ the value at the far rhs of the row represents the absolute spin polarization at the center of the chain. Note that there are two series of values for $\mathcal{N}$ either even or odd. Although there is not enough data to extrapolate to the infinite chain limit, it seems reasonable that both series are separately tending towards the polymer value of 0.463 $|e|$, which is indicative of intermediate diradical character.

Finally, the UHF and LC-UBLYP values for $\alpha$ and $\gamma$ are reported in Table 6, while corresponding UB3LYP and UPBE0 values can be found in SI.

**Table 6: Polarizability and hyperpolarizability values per dimer for the open-shell singlet anti-type periodic phenalenyl polymer obtained with different Hamiltonians. Calculations were performed on both UB3LYP-D and RB3LYP-D optimized geometries.**

| | UB3LYP-D/6-31G* geometry | | RB3LYP-D/6-31G* geometry | |
|---|---|---|---|---|
| Hamiltonian | $\alpha$(a.u.) | $\gamma(\times 10^6)$(a.u.) | $\alpha$(a.u.) | $\gamma(\times 10^6)$(a.u.) |
| UHF | 161.6 | 0.027662 | 161.4 | 0.027036 |
| LC-UBLYP | 340.4 | 2.5678 | 336.3 | 2.2942 |

In the case of UHF the computed $\gamma$ for the polymer is approximately 11 times larger than that reported for the dimer in Table 3, while for the LC-UBLYP functional the corresponding ratio is about 19. LC-UBLYP tends to cure the large overshoot observed in the case of UB3LYP and UPBE0 (see supplementary information). However, the LC-UBLYP $\gamma$ is almost two orders of magnitude greater than the UHF value, which is a rather large electron correlation effect. Nonetheless, in the absence of a correlated wavefunction calculation for the polymer, we utilize the average of the LC-UBLYP and UHF results as a reasonable value for the polymer/dimer ratio (15.0 $\pm$ 4.0 ) and combine that with a UCCSD result for the dimer to obtain our best estimate for the infinite polymer $\gamma$.

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Finite field UCCSD energy calculations for the dimer were carried out with the same basis set, and at the same geometry, as the HF and DFT calculations described above. UCCSD, unlike RCCSD, has been shown to produce a reliable approximation to UCCSD(T) results.[30] After some trial and error we found that a least squares fit of the energy to a quartic power series for the fields 0.0, 1.0, 2.0, 3.0 4.0 and 6.0 (in units of $10^{-3}$ a.u.) could be used to obtain a reliable value of $\gamma = 6.982 \pm 0.014 \times 10^4$ a.u. These fields reproduce the analytical $\alpha$ within 0.3 percent and give $\gamma$ within the error limits cited when any one of the lowest 4 fields is removed from the data set. The fact that the UCCSD static $\gamma$ is intermediate between the UHF and LC-UBLYP values lends support to the procedure we have employed to obtain the polymer/dimer ratio for this property.

Given the UCCSD result quoted above our best estimate for the static second hyperpolarizability of the open shell singlet phenalenyl polymer is $1.0 \pm 0.3 \times 10^6$ a.u. per dimer. For comparison, the MP2 static second hyperpolarizability of polyacetylene along the longitudinal direction[27] is, according to the B-convention,[26] $3.27 \cdot 10^6$ a.u. per -(HC=CH)- unit.

We notice how the enhancement due to stacking is not observed in the case of coronene infinite polymer (cf. Table 4). In this case, the ratio between the *per molecule* second hyperpolarizability in the polymer and in the dimer is only $\approx 4$, almost regardless of the basis set used. In fact, as discussed in the previous section, the larger distance between the monomers allows us in this case to use a diffuse basis set (with upscaled larger exponent), which is also needed due to the smaller cooperative effect of basis functions on neighboring molecules, leading to a stronger basis set dependence that in the case of phenalenyl (cf. Table 1).

# 4    Conclusions

There is considerable interest in the properties of open shell singlet systems. In this paper we have investigated the structure and static second hyperpolarizability, $\gamma$, for an infinite

periodic polymer composed of phenalenyl dimers. Our procedure involved Hartree-Fock and DFT calculations for the isolated dimer and polymer as well as a CCSD treatment of the dimer. The open shell singlet calculations for the polymer were carried out on a modified version of the CRYSTAL14[12] program which, to our knowledge, is the only code with that capability.

At the equilibrium geometry the dimer is, in fact, a closed shell singlet. However, the open shell singlet structure slowly becomes more favorable as the length of an oligomer composed of these dimers is increased. At the same time there is a slow decrease in the alternation of intra- and inter-dimer stacking distances. The cross-over from one structure to the other is estimated to occur for an oligomer consisting of about 40 dimers. In the infinite polymer limit the stacking distance alternation is reduced to essentially zero and the open shell singlet has a very small intermediate diradical character (0.463), which is conducive to producing a high value of $\gamma$. Analogue calculations for a pure closed-shell singlet system (coronene) show much less pronounced enhancement of hyperpolarizability due to the infinite stacking. Conventional UB3LYP and UPBE0 calculations vastly overestimate the static hyperpolarizability of the oligomers and the polymer. On the other hand, an *ab initio* wavefunction treatment, which takes into account electron correlation, is not feasible for these systems. For that reason the following hybrid approach was adopted to determine a best estimate for the polymer. Although it appears that the LC-UBLYP functional may somewhat overestimate the static $\gamma$, the overshoot obtained with UB3LYP or UPBE0 is much reduced. Thus, the ratio between the infinite periodic value of $\gamma$ (per dimer) and the simple dimer value may be approximated as the average of the Hartree-Fock and LC-UBLYP results for this quantity. Then, we used that ratio to scale a UCCSD calculation on the dimer thereby obtaining an estimate of $1.0 \pm 0.3 \times 10^6$ a.u. for the static second hyperpolarizability (*per dimer*) of the infinite periodic chain of open shell singlet phenalenyl dimers.

From our experience with phenalenyl we now have a protocol that can be used in general for estimating second hyperpolarizabilities of open shell singlet diradical polymers. It would

be preferable to have a suitable functional or an ab initio correlated wavefunction method for this purpose. Neither is likely to become available, however, for quite some time. In the case of phenalenyl polymer the static second hyperpolarizability per dimer unit turns out to be comparable to the corresponding value per -(CH=CH)- unit of polyacetylene. It would be worthwhile to compare frequency-dependent properties, such as the dc-Pockels effect and second harmonic generation as well.[31] The former, in particular, may exhibit a large vibrational contribution to the total NLO property that must be taken into account. Other open shell singlet diradical polymers should also be considered.

# 5   Acknowledgment

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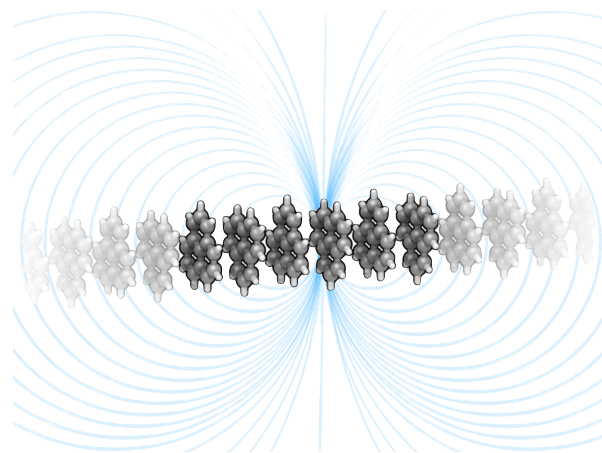
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