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Comment on “How the Number and Location of Lithium Atoms Affect the First Hyperpolarizability of Graphene”

Panagiotis Karamanis* and Claude Pouchan

Groupe de Chimie Théorique et Réactivité, ECP, IPREM CNRS-UMR 5254, Université de Pau et de Pays de l'Adour, Hélioparc Pau Pyrénées 2 avenue du Président Angot, 64053 PAU Cedex 09 – France

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In a recent paper, Hu et al.¹ used “the linear pentacene as a model of the graphene zigzag edge to investigate the effect of the number and location of Li atoms on its hyperpolarizabilities”. In brief, the authors computed the first dipole hyperpolarizabilities of several isomers of lithiated pentacene ($C_{22}H_{14}$) with one up to six lithium atoms fixed on one of its two zigzag edges. Thirteen out of the fourteen different systems considered there were built by replacing one up to five hydrogens of pentacene with Li ($Li_nC_{22}H_{(14-n)}$), whereas the last one, $Li_6C_{22}H_9$, was created from $Li_5C_{22}H_9$ with the addition of one extra Li atom with no further replacement of any hydrogen atom. For this last open shell system (hereafter Li_6 -pentacene), Hu et al. reported an exceptionally large first hyperpolarizability value of 4 501 764 au² at the UBH&HLYP level of theory. According to their text, none of the results concerning the rest of the systems predispose for such a large static hyperpolarizability value. Indeed, out of the 14 systems examined therein by means of density functional theory (DFT), the next larger value belongs to $Li_5C_{22}H_9$ and amounts to only 14 904 au. Therefore, the authors concluded that when one Li atom is attached on the lithiated side of $Li_5C_{22}H_9$ its total first hyperpolarizability increases by a factor of 302.

Although one could reasonably raise serious doubts about the aptness of the specific model for study purposes concerning graphene, both the reported outsized hyperpolarizability enhancement going from $Li_5C_{22}H_9$ to $Li_6C_{22}H_9$ and the magnitude of the reported property itself are intriguingly astonishing. To our knowledge, systems of that size rarely deliver hyperpolarizability values of such a weight. As Hu et al. report, the total first hyperpolarizability of Li_6 -pentacene (as presented in their work) lies orders of magnitudes higher than that in other systems, which have attracted considerable attention owing to their exceptional hyperpolarizable character.

According to the literature, one might indeed experience such a large hyperpolarizability value in cases where loosely bound electrons are involved. Some of the most representative paradigms of such systems are the so-called electron solvated systems³ or ionic salts with electride and alkali characteristics (see ref 4 and references therein). Nonetheless, none of these possibilities is supported by the orbital analysis presented in ref 1. As shown therein, Li_6 -pentacene is closer to a classical donor–acceptor system than to a molecule that implicates loosely bound electrons.

Motivated by this unforeseen effect, we made an effort to understand its source by trying first to reproduce the reported values. During this process, we found that the equilibrium

geometry used by Hu et al. does not correspond to a true minimum of the potential energy hypersurface. In addition, analytic computations of the first hyperpolarizability carried out with the Gaussian 09 suite of programs,⁵ both on this structure and on its true minimum analogue, do not confirm the magnitude of the total first hyperpolarizability presented in ref 1.

We choose to start our commentary from the equilibrium geometry of Li_6 -pentacene. Unfortunately, the authors do not provide in their original article sufficient details in their text about its structure. Of course, one can assume from the pictures provided that most likely a planar structure has been taken into account. However, this cannot be claimed with absolute certainty because only some selected bond lengths and angles are reported (see table 1 of ref 1). In addition, no information concerning the symmetry of this trial system is provided. Therefore, to make direct comparisons, we carried out full geometry optimizations starting from the analogue planar structure of Li_6 -pentacene of an ideal C_{2v} symmetry in which all Li atoms lie on the plane defined by pentacene.

As it is clearly mentioned in ref 1, the geometry of Li_6 -pentacene has been obtained at the UB3LYP level of theory with a Pople's style basis set. More specifically, the authors used the standard augmented and polarized valence triple- ζ 6-311G(3df) and the valence double- ζ 6-31+G(d) basis set for Li and C atoms, respectively (Li :[4s3p3d1f], C :[4s3p1d]). What is not transparent is the basis set used for the H atoms. For this atom, the authors describe the basis set employed as 6-31+G(d). The specific notation, if not a typo, is rather unfortunate and misleading. In Pople's notation for the H atom, the diffuse s-Gaussian type functions are defined as “++”. Also, the widely accepted strategy to polarize an atomic set of H consists of adding p-type Gaussian-type functions first instead of d-type, as it is assumed from the description given in ref 1. Hence, the H basis set used has to be either the nonpolarized 6-31G⁶ ([2s]) set or the augmented polarized 6-31++G** ([3s1p]) set. For the sake of simplicity, hereafter we shall be referring to these basis sets as A0 and A1, respectively, thus, A0 \equiv Li:6-311G(3df)/C:6-31+G(d)/H:6-31G and A1 \equiv Li:6-311G(3df)/C:6-31+G(d)/H:6-31++G**.

As seen in Table 1 an absolute match is found between the structural data presented in ref 1 and the optimized geometry

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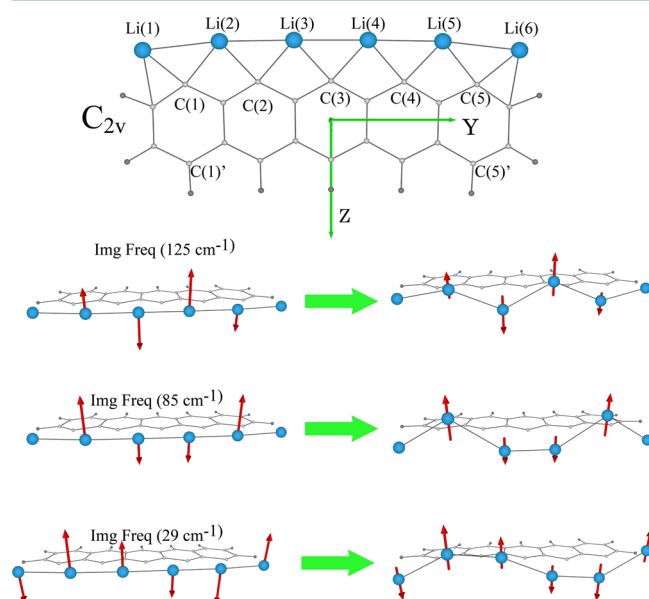
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Table 1. Comparison between the Structural Data of $\text{Li}_6\text{C}_{22}\text{H}_9$ As Reported in Reference 1 and Those Found Here^a

	$\text{Li}_6\text{C}_{22}\text{H}_9^b$	$\text{Li}_6\text{C}_{22}\text{H}_9\text{-C}_{2v}^c$	$\text{Li}_6\text{C}_{22}\text{H}_9\text{-C}_2^d$
C(1)–Li(1)	1.93	1.929 (1.928)	1.945
C(2)–Li(2)	1.99	1.990 (1.990)	1.989
C(3)–Li(3)	1.97	1.965 (1.966)	1.973
C(4)–Li(4)	1.96	1.962 (1.962)	1.977
C(5)–Li(5)	1.97	1.967 (1.967)	1.991
C(5)–Li(6)	1.93	1.929 (1.928)	1.949
C(1)–C(5)	10.06	10.066 (10.064)	9.976
C(1)′–C(5)′	9.80	9.800 (9.800)	9.852
θ	76	76.4 (76.3)	79.4

^aGeometry optimization has been performed at the UB3LYP level with the application of A0 \equiv Li:6-311G(3df)/C:6-31+G(d)/H:6-31G and A1 \equiv Li:6-311G(3df)/C:6-31+G(d)/H:6-31++G** basis sets. All distances are given in angstroms and angles in degrees. ^bSelected bond-lengths and angle reported by Hu et al.¹ ^cMatching bond lengths and angle of the planar C_{2v} structure found in this work with the A0 and A1 (values in parentheses) basis set. ^dEquivalent bond lengths and angle of the C_2 structure found in this work at the B3LYP/A0 level.

we found at the B3LYP with both of the above basis sets. Hence, beyond any doubt the authors considered a planar structure at least very similar to the one shown in Figure 1

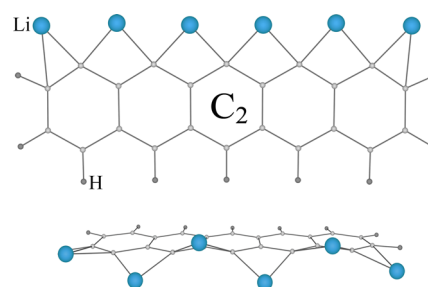
**Figure 1.** Molecular structure of $\text{L}_6\text{-pentacen-C}_{2v}$ optimized at the UB3LYP/A0 level of theory and displacement patterns of the three imaginary frequencies found at the same level of theory.

belonging to the C_{2v} symmetry group point. To check the type of the planar stationary point, we carried out extensive analytic frequency computations on its equilibrium geometry. The obtained results revealed that the specific configuration corresponds in fact to a higher order saddle point characterized by three imaginary frequencies. At the UB3LYP/A0 (A1) level, the strongest of those amounts to 125i (126i) cm^{-1} , whereas the rest of the two frequencies amount to 85i (84i) and 29i (25i) cm^{-1} . This result is also confirmed by geometry optimizations at the Hartree–Fock (UHF), UBLYP, UBPW91, and UB3PW91 levels with the same and several larger basis sets. At this point, we must stress that when the

geometry optimization is repeated with no symmetry constraints one may obtain a structure of C_s symmetry very close to the C_{2v} . The two structures are practically equivalent (the C_s configuration is ~ 0.08 kcal/mol lower in energy) and bear three imaginary frequencies of almost the same magnitudes. Therefore, one can safely view that the C_s configuration as slightly distorted C_{2v} structure.

To bear out the reliability of the obtained result, we performed the wave function stability test that is provided by Gaussian 09 for both the UB3LYP/A0 and UB3LYP/A1 wave functions. In both cases, no instability issues were detected. At this point, it must be also noted that the spin contamination that might prove crucial for the accuracy of obtained results is negligible for all DFT methods used ($S^2 = 0.751$ with an expectation value for the doublet of 0.75), whereas it is found to be stronger in the case of Hartree–Fock wave function ($S^2 = 0.8$).

The displacement patterns shown in Figure 1 point out that all imaginary frequencies drive the edge Li atoms out of the plane defined by the rings of pentacene. This inevitably forces the C_{2v} structure to collapse to a nonplanar configuration of lower symmetry. This is further verified by full geometry optimization at the UB3LYP/A0 level, taking into account the displacement patterns of all three imaginary frequencies (one at a time) without any symmetry restrictions. Each of the three distortion patterns pushes the C_{2v} structure of $\text{L}_6\text{-pentacene}$ downhill, and the initial configuration relaxes straightforwardly or through a first-order saddle point to the quasi-planar local minimum of C_2 symmetry shown in Figure 2. As seen in Table 1, the structural data corresponding to the $\text{L}_6\text{-pentacene-C}_2$ true minimum are notably different from those corresponding to the structure used in ref 1.

**Figure 2.** Molecular structure of $\text{L}_6\text{-pentacen-C}_2$ optimized at the UB3LYP/A0 level of theory.

To validate further the above outcome, we carried out structural optimizations on larger heavily lithiated polycyclic acenes, which in their hydrogenated form are utilized lately as models in computational studies involving graphene nano-flakes.⁷ The fully optimized structures given in Figure 3 prove that such types of distorted structures are not only limited in partially lithiated acenes such as the one negotiated in ref 1. In fact, this is the general situation in all sorts of fully lithiated zigzag species we considered regardless of their shape or size. The source of the occurring induced distortion can be trivially attributed to coulomb repulsion, which obliges the neighboring positively charged Li atoms to maximize their mutual distances. A more elegant interpretation of the observed unambiguous “symmetry breaking” might also be given though the prism of pseudo-Jahn–Teller theory.^{8,9}

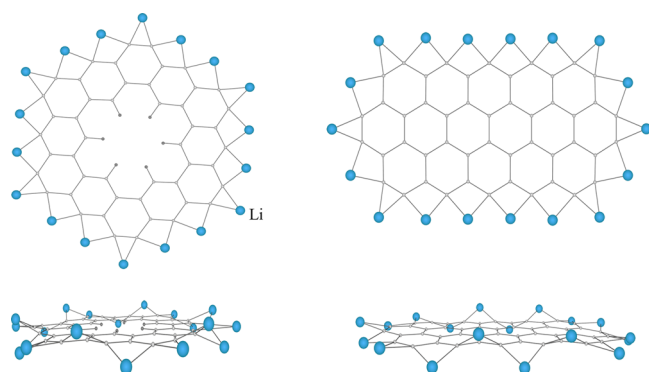


Figure 3. Molecular structures of two representative examples of fully lithiated graphene flakes optimized at the B3LYP/6-31G(d) level of theory.

Up to this point, it is demonstrated that beyond any doubt the structure considered in ref 1 does not offer for a reliable ground-state property study of Li_6 -pentacene. Nevertheless, the small energetic difference (~ 4 kcal/mol) and the structural similarity between the higher order saddle point of C_{2v} symmetry and the local minimum of C_2 may cause insignificant changes in the computed hyperpolarizabilities. Therefore, fueled by pure scientific curiosity, we carried out analytic hyperpolarizability computations with a number of different density functionals first on the planar Li_6 -pentacene considered in ref 1. To make direct comparisons, we used the same basis set it is assumed¹⁰ that Hu et al. chose in their work.

As seen in Table 2, depending on the method used, the total first hyperpolarizability of Li_6 -pentacene- C_{2v} varies from (9.4 to

Table 2. Analytic Values of the Dipole (Hyper)polarizability Tensorial Components (β_{zzz} , β_{xxz} , β_{yyz}) and Total First Hyperpolarizability (β_{tot}) of Li_6 -pentacene- C_{2v} Computed with Various Density Functionals and the A0 Basis Set^a

method	β_{zzz}/au	β_{xxz}/au	β_{yyz}/au	$\beta_{\text{tot}}/\text{au}$
UBH and HLYP ^b	−8.7	−4.6	−3.8	17.1
UB3PW91	−12.5	−2.7	−5.7	20.9
UB3LYP	−10.4	−1.4	−17.1	29.0
UBPW91	−11.3	−1.0	1.3	11.0
UBLYP	−1.6	−12.2	−10.7	24.5
CAM-UB3LYP	−8.4	−1.7	−2.6	12.7
LC-UBLYP ($\mu=0.47$) ^c	−7.0	−1.2	−1.2	9.4
LC-UBLYP ($\mu=0.33$)	−9.0	−2.0	−1.8	12.8

^aAll values have been divided by 10^3 . ^bAt this level of theory, the corresponding quantities with basis set A1 are: $\beta_{zzz} = -11.5 \times 10^3$, $\beta_{xxz} = -4.9 \times 10^3$, and $\beta_{yyz} = -1.5 \times 10^3$ au. ^c μ stands for the range separating parameter of the LC scheme. 0.47 is the default for Gaussian 09.

$29) \times 10^3$ au. Obviously, there is a strong deviation between the applied DFT methods in the prediction of the total first hyperpolarizability. Such a method performance is routinely met in alkali metal ionic salts (see for instance ref 11). However, none of those widely used DFT methods predicts that this specific ionic salt, even at the unstable planar configuration, can be characterized by the exceptionally large first total hyperpolarizability reported in ref 1. For instance, the same method used in ref 1, namely, UBH&HLYP, suggests that the total first hyperpolarizability of Li_6 -pentacene- C_{2v} amounts to 1.7×10^4 au instead of 4.5×10^6 . Furthermore, even at the

UB3LYP/A0 method, which as Hu et al. correctly state yields somewhat oversized hyperpolarizabilities, the computed analytic values are still orders of magnitude smaller than the one reported in their study.

Interestingly enough, the analytically obtained hyperpolarizability at the UBH&HLYP/A0 level of theory now fits properly with the results reported for the rest of the species investigated in ref 1. For instance, the difference in β_{tot} between the most hyperpolarizable isomer of Li_5 -pentacene reported by Hu et al. and its lithiated counterpart now amounts to $\sim 3 \times 10^3$ au instead of 4×10^6 au. Consequently, the evolution of the first hyperpolarizability as a function of the number of Li atoms is in fact smooth and definitely more reasonable. This finding contrasts the conclusions of ref 1, which suggests the opposite.

To shed some more light on this subject, we explored the magnitude of the first hyperpolarizability of the true local minimum of C_2 symmetry we found in this work. For this task, we carried out some trial computations at the UHF level of theory. This time, though, we chose more reasonable¹² basis sets than A0 and A1 for both the geometry and property computations. All results of the successful attempts are presented in Table 3. As seen, the predicted total first

Table 3. Analytic Values of the Dipole (Hyper)polarizability Tensorial Components (β_{zzz} , β_{xxz} , β_{yyz}) and Total First Hyperpolarizability (β_{tot}) of Li_6 -pentacene- C_2 Computed at the UHF Level with Various Basis Sets^a

basis set	β_{zzz}/au	β_{xxz}/au	β_{yyz}/au	$\beta_{\text{tot}}/\text{au}$
6-311++G(2d,2p)	−21.0	−39.7	−3.9	64.6
6-31++G(d,p)	−36.3	−15.9	−4.2	56.4
cc-p-VDZ	−12.6	−33.6	−3.3	49.5 ^b
cc-p-VTZ	−17.8	−34.5	−2.6	54.9 ^c

^aAll values correspond to the UB3LYP/6-311G** of optimized geometry Li_6 -pentacene- C_2 and have been divided by 10^3 . ^bAt UBH&HLYP level $\beta_{\text{tot}} = 42.0 \times 10^3$ au. ^cAt UBH&HLYP level $\beta_{\text{tot}} = 49.7 \times 10^3$ au.

hyperpolarizabilities, although interestingly large, still lie about two orders of magnitude lower than the one reported by Hu et al. Similar results have also been obtained with the UBH&HLYP functional.

To conclude, we have demonstrated that the strikingly outsized hyperpolarizability enhancement reported by Hu et al. after one Li atom is adsorbed on the one side of penta-lithiated pentacene is erroneous. Sufficient evidence has been provided showing that the configuration of Li_6 -pentacene used by these authors is not a true minimum. What's more, no sizable hyperpolarizability augmentation such as the one described in ref 1 is supported by analytic DFT hyperpolarizability computations. Consequently, the evolution of the first hyperpolarizability of lithiated pentacene as a function of the number of Li atoms becomes vastly less impressive compared with the one presented and discussed by Hu et al. As suggested by the obtained results, the source of the extremely large reported hyperpolarizability value reported in ref 1 has no connection to the considered planar structure symmetry and most likely is related to the computational procedure¹³ followed. From our point of view, more work is needed to investigate further the electric properties of such species, especially when such studies aim at predicting properties of more complex systems (e.g., graphene). In this case, any future

attempts should be focusing on physically more reasonable models, a task that is far from the scope of this Comment.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pkaraman@univ-pau.fr.

Notes

The authors declare no competing financial interest.

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(10) Although the authors clearly state that for the geometry optimization the A0 (or A1) basis set was used this is not evident for the computations of the first hyperpolarizability, and thus it is assumed that in their computations one of the above basis sets has been utilized.

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(12) For Li atoms, which, as Hu et al. show, are characterized by strongly positive atomic charges, the choice of a heavily polarized

triple- ζ set cannot be easily justified, especially when in the same set the carbon atoms of L₆-pentacene, which receive the negative charge lost from Li, are approximated by a double- ζ basis set with only one (tight in this case) polarization function.

(13) The authors used the Gaussian 03 suite of programs in their study. The specific version does not provide analytic first hyperpolarizability values at the Bh&LYP level of theory. Thus, because no information is provided it must be guessed that the reported results of ref 1 have been obtained either through a double numerical differentiation of energies or by numerical differentiation of the corresponding analytic polarizabilities (the widely known finite-field technique). Accordingly, in an attempt to shed some light on the source of the reported result, we computed the hyperpolarizabilities of Li₆-pentacene with Gaussian 09 using both of the above options. In both cases the obtained results confirmed the analytically predicted ones.