A comparative study of the static third-order polarizabilities of bowl/non-cage to cage structures: a structure–property correlation study

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The average static third-order polarizabilities (γ) have been computed for the bowls and cages having the same number of carbon atoms. The bowls have higher (γ) than their corresponding cages. The dependence of (γ) on the average pyramidalized angle (θa) and maximal length L can be deduced. Near cages, having a window (C_{32} isomers), are capped with C_6 to generate five isolated pentagon rule (IPR) isomers of C_{78} fullerenes following a circumscribing algorithm. The (γ) values for the C_{78}’s and C_{72}’s are correlated with (θa) and L. The change in (γ) from C_{72}’s to C_{78}’s are correlated with a local parameter like the capped angle (α).

1. Introduction

The conjugated and delocalized nature of the π electronic structure implicates a very strong polarizability and hyperpolarizability along the carbon skeleton. It is well known that these materials are likely candidates for the components of technological devices owing to their large third-order nonlinear behaviour. Relationships between molecular structure and the magnitude of the nonlinear optics (NLO) response is of singular importance for the rational design of the new and improved materials [1]. A survey of the literature reveals that many attempts have been made to establish a definite relationship between third-order polarizability γ and the structural parameters [2–11]. After the pioneering work of Rustagi and Ducci [12] a number of theoretical and empirical correlations between γ and the conjugated length n have been proposed for oligomeric linear molecules such as polyenes [3–11]. Different levels of theory predict, for small values of n, a power law dependence of the type γ ∝ n^a, where 3 < a < 6. Both theoretical and experimental studies have shown that for larger linear polymers a saturation regime is entered, where a ∼ 1. In polycylenes this occurs at ∼120 carbon atoms [13] and for oligothiophenes it has been shown to occur at 7 or 8 rings [14].

The advancing technology for the production of bulk quantities of fullerenes [15, 16] has provided another interesting class of completely conjugated materials. Associated with the delocalized π conjugated electrons in fullerenes, their large nonlinear optical responses have been the subject of several recent experimental studies [17–25]. A large quantity of experimental data concerning third-order optical nonlinearities have been accumulated for the fullerenes C_{60}, C_{70} and C_{84}. Also it has been noted that γ increases from C_{60} to C_{70} and to C_{84} [26]. When comparing the more diverse hydrocarbons, γ/n_n could be used [27, 28], where n_n refers to the number of π electrons. These comparisons indicate that, for a particular number of conjugated carbon atoms, γ has been found to be larger for linear polymers (quasi-1-dimensional) than for other systems. Hence, no coherent and synthetically useful picture has been obtained to relate γ/n_n with the structural parameters for the different classes of molecules. Thomas [29] has made an attempt to correlate γ with n_n and surface area for curved aromatic molecules. Further, Fanti et al. [30, 31] have proposed a scaling law to predict γ considering γ_C_{60} as the reference molecule. Unfortunately, these scaling laws and all the empirical relations suggested earlier are not good enough to predict γ or to correlate γ very accurately with the structural parameters for the isomeric molecules [31]. In fact, there have been attempts to correlate γ with the optical gaps [32, 33] for the five C_{78} isolated pentagon rule (IPR) isomers. It may be pointed out that no unique correlation between γ and the structural parameters for this diverse class of molecules has been suggested so far. Further.
correlation becomes more tedious if one considers the isomeric molecules. Recently, Moore et al. [34] have proposed that $\gamma$ for a carbon-cage fullerene does depend on a combination of the number of aromatic rings and the cage length.

In this paper we have considered two classes of molecule. First, we have taken into consideration of the bows and their respective cages (C$_{20}$ to C$_{40}$). The bows are generated following the pentagon road (PR) proposed for the fullerene generation mechanism [35]. At the outset, C$_{20}$ (PR) is considered, where a pentagon is surrounded by five hexagons, and the C$_2$ components are gradually put at the rim of the growing cluster as proposed by Bates and Scuseria [35] in order to have PR structures (bows). The static third-order polarizabilities $\gamma$ of the bows and their respective cages are then computed. Next we have considered the five C$_{72}$ isomer (non-cage) structures which are capped by C$_6$ to form five IPR isomers of C$_{78}$ fullerenes following a circumscribing algorithm [36] which is akin to the kinetic ring stacking model of Achiba et al. [37]. The $\gamma$ values of C$_{72}$’s and C$_{78}$’s are computed. It may be mentioned that the C$_{72}$’s are almost curves and have one open window [38]. However, six carbon centres have dangling bonds, and a C$_6$ can cap the C$_{72}$. Here, in this study, first we have tried to compare the $\gamma$ of bows and cages for the same number of carbon atoms (C$_{20}$ to C$_{40}$), and second the changes in $\gamma$ from non-cage to cage structures (C$_{72}$ to C$_{78}$) are correlated with structural parameters like the pyramidalized angles ($\Theta_p$) [39] and the capped angles ($\alpha$).

The capping technique seems to depict a more local phenomenon than the global one [40]. Although the final cage formation through capping could cause certain changes at all the centres, the changes in the capped centres are more pronounced. A recent investigation of Geskin and Bredas [41] proposes an interesting observation about the local orbital contribution to cubic polarizabilities $\gamma$. The $\gamma$ values calculated by a sum-over-states (SOS) [42] and a finite field derivative approach [43] have been considered a global property of the whole molecule [41]. These workers [41] have presented the contribution from the local and global terms for an extended polynene system and shown that the terminal and the inner parts of a long polynene chain play crucial roles in the determination of $\gamma$.

2. Computational background

The finite-field (FF) method developed by Kurtz et al. [44] has been used to calculate the molecular polarizabilities and hyperpolarizabilities. All valence electron calculations using the semiempirical Hamiltonian AM1 having been employed to obtain polarization under different static electric fields. The implicit static field is inserted within the Hamiltonian as outlined by Williams [45]. The tensor components for polarizabilities and hyperpolarizabilities are obtained through the FF procedure. The AM1/FF is already implemented within the ‘Mopac’ program [46] and the details of the FF method for calculating the static third-order polarizabilities has been described [44]. The response of a molecule to a homogeneous static electric field could be expanded in two different forms: e.g. (i) energy expansion and (ii) dipole moment expansion.

$$U(E) = U^0 - \sum \mu_i E_i - \frac{1}{4} \sum \alpha_{ij} E_i E_j - \frac{1}{4} \sum \beta_{ijk} E_i E_j E_k$$

$$- \frac{1}{4} \sum \gamma_{ijkl} E_i E_j E_k E_l , \ldots$$

$$\mu_i(E) = \mu_i^0 + \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_k E_l$$

$$+ \sum \gamma_{ijkl} E_k E_l , \ldots$$

Here, $U^0$ is the energy in the absence of the field, $\mu_i^0$ is the dipole in the absence of the field, $E_i$ is the applied field, $\alpha_{ij}$ is the polarizability tensor, $\beta_{ijk}$ is the second-order polarizability tensor, $\gamma_{ijkl}$ is the third-order polarizability tensor, etc. These series have equivalent coefficients if the Hellmann–Feynman theorem [23] is obeyed, since $\mu_i = -\partial U/\partial E_i$. The orientationally averaged third-order polarizability can be expressed at zero frequency as

$$\langle \gamma \rangle = \frac{1}{3}[\gamma_{xxx} + \gamma_{yyy} + \gamma_{zzz} + 2(\gamma_{xxy} + \gamma_{xyx} + \gamma_{xyz})].$$

The numerical stability of the finite field equations is sensitive to the accuracy of the energy and dipole moment calculations. To reduce the numerical instability of the calculations of the third-order polarizability terms, the value of the electric field strength should be selected with much care. The energy expression is used in the present work and the field strength chosen to be 0.0014 au, which minimizes the numerical instabilities and also prevents the inclusion of the higher order terms in the energy expression.

3. Results and discussion

We have computed $\gamma$ for the bows and cages for the C$_{20}$ to C$_{40}$ clusters. The heat of formation $\Delta H_f$, the HOMO–LUMO gap $\Delta E_g$, the averaged pyramidalized angle $\langle \Theta_p \rangle$, maximum length L in between the two carbon centres and, finally, the values of $\langle \gamma \rangle$ are presented in table 1. It should be pointed out that $\langle \Theta_p \rangle$ for the bows are calculated by neglecting the carbon centres having dangling bonds. It should be noted further that before the $\gamma$ calculations, the geometries of the clusters are completely optimized with force calculations. There is no imaginary vibrational frequency for any of the above clusters. The behaviour of $\gamma$ (table 1) is most interesting: the values are reduced from bowl
Table 1. \(\langle \gamma \rangle, \Delta E_g, \langle \Theta_p \rangle\) and \(L\) for the non-cage and cage clusters \((\langle \gamma \rangle\) is in \(10^{-36}\) esu, \(\Delta E_g\) is in eV, \(\langle \Theta_p \rangle\) is in deg, and \(L\) is in Å).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\langle \gamma \rangle)</th>
<th>(\Delta E_g)</th>
<th>(\langle \Theta_p \rangle)</th>
<th>(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C20 bowl</td>
<td>11.3825</td>
<td>7.8469</td>
<td>5.7137</td>
<td>6.3601</td>
</tr>
<tr>
<td>C20 cage</td>
<td>12.7129</td>
<td>5.8732</td>
<td>20.9032</td>
<td>4.1708</td>
</tr>
<tr>
<td>C24 bowl</td>
<td>80.3228</td>
<td>4.1421</td>
<td>5.8175</td>
<td>8.0855</td>
</tr>
<tr>
<td>C24 cage</td>
<td>5.30051</td>
<td>6.26</td>
<td>19.0096</td>
<td>4.671</td>
</tr>
<tr>
<td>C26 bowl</td>
<td>128.4723</td>
<td>4.6962</td>
<td>8.1212</td>
<td>7.8472</td>
</tr>
<tr>
<td>C26 cage</td>
<td>9.6031</td>
<td>5.7507</td>
<td>18.1733</td>
<td>5.2377</td>
</tr>
<tr>
<td>C28 bowl</td>
<td>238.0657</td>
<td>5.2614</td>
<td>8.1238</td>
<td>7.8796</td>
</tr>
<tr>
<td>C28 cage</td>
<td>12.605</td>
<td>5.7507</td>
<td>17.3946</td>
<td>4.9389</td>
</tr>
<tr>
<td>C30 bowl</td>
<td>33.927</td>
<td>7.1803</td>
<td>8.3484</td>
<td>7.7672</td>
</tr>
<tr>
<td>C30 cage</td>
<td>15.4451</td>
<td>5.5873</td>
<td>16.8491</td>
<td>5.3074</td>
</tr>
<tr>
<td>C34 bowl</td>
<td>34.7422</td>
<td>6.4914</td>
<td>9.0887</td>
<td>7.9141</td>
</tr>
<tr>
<td>C34 cage</td>
<td>22.7912</td>
<td>5.4819</td>
<td>15.9139</td>
<td>5.8296</td>
</tr>
<tr>
<td>C38 bowl</td>
<td>42.0834</td>
<td>6.1757</td>
<td>9.6081</td>
<td>7.834</td>
</tr>
<tr>
<td>C38 cage</td>
<td>11.9341</td>
<td>14.9156</td>
<td>5.7562</td>
<td></td>
</tr>
<tr>
<td>C40 bowl</td>
<td>41.9207</td>
<td>5.7749</td>
<td>10.0032</td>
<td>7.7404</td>
</tr>
<tr>
<td>C40 cage</td>
<td>33.6311</td>
<td>4.7828</td>
<td>14.6757</td>
<td>6.8158</td>
</tr>
</tbody>
</table>

To cage structures except for the C20 case. The C20 cage has only pentagons and these pentagons might be playing some roles in increasing the value of \(\gamma\) from its bowl which contains five hexagons and single pentagon. When we try to compare \(\Delta E_g\) with \(\gamma\), we note that there exists an inverse relationship between the \(\Delta E_g\) and \(\gamma\) up to C28, but from C30 onwards there is a reverse trend. Hence, there is no unique correlation between \(\gamma\) and \(\Delta E_g\). On the other hand, there is a good correlation between \(\langle \Theta_p \rangle\) and \(\gamma\) and between \(L\) and \(\gamma\) except for the C20 case. With increase in \(\langle \Theta_p \rangle\) from bowl to cage, \(L\) and \(\gamma\) decrease. Hence, one can say that \(L\) and \(\langle \Theta_p \rangle\) are definitely controlling the \(\langle \gamma \rangle\). After establishing a relationship between \(\langle \gamma \rangle\), \(\langle \Theta_p \rangle\) and \(L\), we have conducted a case study for the five IPR structures of the C78 fullerenes, considering their formation from C72 non-cage isomers (Figure 1). We have computed \(\langle \Theta_p \rangle\), overall curvature \(\sum \Theta^2\), spread over POAV1 angles [39], maximum length \(L\), angles CCC before and after capping \(\langle \alpha \rangle\), Connolly surface area [47] \(S\) with a probe radius equal to 0.1 Å along with \(\langle \gamma \rangle\) for C72's, C78's, as given in Table 2.

The five topologically distinct IPR isomers of C78 are labelled 1 (D3h), 2 (D3h), 3 (D3), 4 (C2v), and 5 (C2v) and their corresponding C72 isomers are labelled 1'-5'. While advocating the polyhedral model over the spherical one for fullerene cages, Haddon [48] has given a correlation between the curvature and the pyramidalized carbon atoms. In fact, he has proved with high accuracy that the pyramidalization angles and the curvatures at conjugated carbon atoms are directly proportional. It is well known that due to their shell structures, the curved connections among the carbon centres in the curved aromatic molecules [29] could cause the misalignment of the two \(\pi\) orbitals at the adjacent carbon atoms in the path of conjugation and somewhat reduce the \(\pi\) orbital overlap and aromaticity. On the other hand, it may be expected that the 3D \(\pi\) conjugation might provide extra conjugation due to the electron propagation. However, the local curvature [48] present in the curved aromatic molecules reduces the local conjugation. The relationship between \(\gamma\) and the conjugation length \(n\) has been studied in the case of oligomeric linear molecules such as polynyes [3-11]. Thomas [29] correctly pointed out that the conjugation length becomes ill-defined in the case of the higher dimensional molecules, and preferred to propose the correlation of \(\gamma\) with a measurement of high

Table 2. \(\gamma\) and structural data for C78 and C72.a

<table>
<thead>
<tr>
<th>Isomers</th>
<th>(\gamma)</th>
<th>(L)</th>
<th>(\langle \Theta_p \rangle)</th>
<th>(\Theta_{\max})</th>
<th>(\Theta_{\min})</th>
<th>(\sum \Theta^2)</th>
<th>(S)</th>
<th>(\alpha^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52.82</td>
<td>9.129</td>
<td>10.364</td>
<td>12.126</td>
<td>6.569</td>
<td>2.655</td>
<td>459.61</td>
<td>118.6</td>
</tr>
<tr>
<td>1'</td>
<td>57.40</td>
<td>8.918</td>
<td>9.599</td>
<td>12.097</td>
<td>6.051</td>
<td>1.942</td>
<td>479.418</td>
<td>117.8</td>
</tr>
<tr>
<td>2</td>
<td>81.62</td>
<td>8.526</td>
<td>10.230</td>
<td>11.730</td>
<td>8.596</td>
<td>2.508</td>
<td>458.447</td>
<td>121.6</td>
</tr>
<tr>
<td>2'</td>
<td>87.95</td>
<td>8.324</td>
<td>9.817</td>
<td>11.708</td>
<td>7.130</td>
<td>1.973</td>
<td>470.847</td>
<td>121.1</td>
</tr>
<tr>
<td>3</td>
<td>54.61</td>
<td>9.091</td>
<td>10.323</td>
<td>12.006</td>
<td>6.504</td>
<td>2.606</td>
<td>460.770</td>
<td>118.6</td>
</tr>
<tr>
<td>4</td>
<td>56.05</td>
<td>8.982</td>
<td>10.308</td>
<td>12.261</td>
<td>6.452</td>
<td>2.594</td>
<td>460.904</td>
<td>105.9</td>
</tr>
<tr>
<td>4'</td>
<td>72.91</td>
<td>8.970</td>
<td>9.300</td>
<td>12.329</td>
<td>5.206</td>
<td>1.826</td>
<td>509.209</td>
<td>102.9</td>
</tr>
<tr>
<td>5</td>
<td>67.82</td>
<td>8.755</td>
<td>10.263</td>
<td>12.284</td>
<td>7.278</td>
<td>2.545</td>
<td>458.840</td>
<td>108.8</td>
</tr>
<tr>
<td>5'</td>
<td>102.92</td>
<td>8.639</td>
<td>9.742</td>
<td>12.265</td>
<td>6.534</td>
<td>1.974</td>
<td>480.296</td>
<td>121.0</td>
</tr>
</tbody>
</table>

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a Units: \(\gamma\) is in \(10^{-36}\) esu, \(\langle \Theta_p \rangle\), \(\Theta_{\max}\), \(\Theta_{\min}\) and \(\alpha\) are in deg, \(\sum \Theta^2\) is in rad, \(L\) is in Å, and \(S\) is in Å².

b Two different capped angles are there in 3–5 and 3'–5'.

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dimension such as surface area. Unfortunately, this correlation also fails to account for the good correlation in the isomeric system under investigation (table 1).

When we looked at the $\gamma$ and the $\langle \Theta_p \rangle$ values for the C$_{78}$ IPR isomers, we noted an excellent correlation between them. It may be observed that with decrease in $\langle \Theta_p \rangle$ the value of $\gamma$ increases, proving clearly that the most spherical IPR, 2 [49], has the maximal $\gamma$ followed by 5. This study proves that there exists a good correlation between $\langle \gamma \rangle$ and $\langle \Theta_p \rangle$ as proposed earlier by taking C$_{34}$ to C$_{40}$ cages. For the five isomeric C$_{78}$ cage structures, $\langle \Theta_p \rangle$ and L are directly proportional to each other and the relationship between $\gamma$ and $\langle \Theta_p \rangle$ follows the same trend as given by $\langle \Theta_p \rangle$. It is interesting to note, based on the $\langle \Theta_p \rangle$ and $\sum \Theta_p$ results, that the spherical character of the five isomers of C$_{78}$ is in the order 2$'$ $<$ 5$'$ $<$ 1$'$ $<$ 3$'$ $<$ 4$'$. We have shown earlier that the most non-spherical geometry attains the most spherical geometry after capping [50]. Hence, one can assume that the change in $\gamma$ should follow the same pattern. In fact, it does not follow the same trend but rather it prefers the order 5$'$.4$'$ $>$ 3$'$ $>$ 4$'$ $>$ 2$'$ $>$ 1$'$. Hence, one may conclude that though the increase in $\langle \Theta_p \rangle$ decreases $\gamma$ in each individual case, the change in $\gamma$ does not follow the same pattern as that of $\langle \Theta_p \rangle$. Earlier, $\Theta_p$ has been shown to provide a useful index of the degree of non-planarity, a measure of local curvature and of the strain at the individual carbon centres in fullerenes [48]. We would like to point out that if $\Theta_p$ is good enough to depict the local geometry completely, then also it should project the change in the conjugation before and after capping and should have a good correlation with the change in the $\gamma$ values. However, for the system in question the change in the $\Theta_p$, i.e., $\Delta \langle \Theta_p \rangle$, and the change in $\gamma$, i.e., $\Delta \gamma$, do not correlate well. Hence, we feel that although there is an excellent correlation between $\langle \Theta_p \rangle$ and $\gamma$ for the cage structures, the same type of correlation does not exist for the non-cage structures for the isomeric cases. Then, in order to understand the change in $\gamma$ after capping, we have considered only the geometry of the atoms concerned, those which are really involved in the capping process. Figure 1 indicates that in all the C$_{72}$ isomers six carbon centres have dangling bonds and are capped by C$_6$. These capped angles $\alpha$ before and after capping are calculated and are given in table 2. It is observed that the change in the capped angles is in the order 5$'$.5$'$.3$'$.2$'$.1$'$. Hence, this trend only supports the change in $\gamma$ except for the last two cases. Hence, we may say that a more involved local term like the capped angles could indicate the change in $\gamma$. However, the deviation observed lower down the scale may be due to the involvement of some other global terms controlling $\gamma$.

This study reveals that $\langle \gamma \rangle$ does depend on $\langle \Theta_p \rangle$ and L for the cage structures. The capping technique reduces $\gamma$ when the non-cage structures are capped to generate the cage structures. However, the change in $\gamma$ from C$_{72}$ to C$_{78}$ could not be correlated with $\langle \Theta_p \rangle$ and L, but could
have a reasonably good correlation with a more involved local term like the capped angles. Again, this study corroborates the ideas given by Geskin and Brédas [37] regarding the difficulty in having one excellent correlation between $\gamma$ and one unique structural parameter. Further, it may be concluded that the supposed global molecular property ($\gamma$) could have a local prospective when the system changes from a non-cage to a cage structure.

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References