
$C_{60}(NO_2)_2$: QUANTUM-CHEMICAL EVALUATIONS OF
STRUCTURE, ENERGETICS, AND VIBRATIONAL SPECTRA

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ABSTRACT
The complete PM3 structural optimizations are reported for all 23 positional isomers of $C_{60}(NO_2)_2$ and interesting symmetry reductions are found. There are two low energy structures while all the remaining species are separated by more than 10 kcal/mol from the computed ground state. In the ground state the two nitro groups are placed in para position on one hexagon. The next lowest structure is produced by addition to one 6/6 (double) bond
of the cage. The species highest in energy are separated by more than 50 kcal/mol from the ground state. IR vibrational spectra are also predicted for the low-energy structures.

INTRODUCTION

Numerous fullerene derivatives have already been produced,\textsuperscript{1–6} based not only on C\textsubscript{60} but on other fullerene cages, too. In fact, the process of fullerene functionalization started almost immediately after the fullerene synthesis. The process has constantly been assisted and supported also by quantum-chemical computations.\textsuperscript{7–10} Among the various chemically-modified fullerenes already available, multi-nitro and multi-hydroxy (fullerols or fullerols) derivatives\textsuperscript{11–25} of C\textsubscript{60} represent an important, distinguished class of fullerene compounds, even with a demonstrated application potential.\textsuperscript{17} Actually, the two sets of derivatives are closely inter-related as polyhydroxylated fullerenes can be produced\textsuperscript{20} by hydrolysis of polynitro-fullerenes. Polynitro-fullerenes can simply be prepared\textsuperscript{13} by additions of nitrogen dioxide radicals to the fullerene cage. In fact, even a straightforward nitration with dinitrogen tetroxide produces\textsuperscript{22} the nitro-derivatives. Clearly enough, complex mixtures of derivatives are typically produced. Polyhydroxylated fullerenes have a wide spectrum of applications. Their solubility in water or polar organic solvents is increased\textsuperscript{17} significantly if the number of hydroxy groups per cage reaches over 15. Fullerols have been for ex-
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ample used\textsuperscript{15-17} for production of star-shaped polymers, and they also have interesting applications in medicine.

This paper deals with dinitro-derivatives of C\textsubscript{60}. Molecular structure of C\textsubscript{60}(NO\textsubscript{2})\textsubscript{y} (similarly to C\textsubscript{60}(OH)\textsubscript{x}) is virtually unknown. Polynitro-derivatives should be somewhat easier to handle as the observed average number\textsuperscript{22} is four nitro groups per fullerene molecule (compared to 10-20 OH groups\textsuperscript{17} in multi-hydroxy derivatives). Hence, in this paper we report quantum-chemical semiempirical computations of all structural isomers of C\textsubscript{60}(NO\textsubscript{2})\textsubscript{2}. The report represents a continuation of our previous computations\textsuperscript{21,23,25}

COMPUTATIONS

Computational studies of molecular systems with high numbers of atoms and low or no symmetry are still performed\textsuperscript{26-28} in the most efficient way by semiempirical rather than \textit{ab initio} quantum-chemical methods. The computations reported in this paper were indeed performed with the standard version of the PM3 semiempirical method.\textsuperscript{26} However, at early stages the AM1 method\textsuperscript{27} was applied, too. This choice was helpful if the PM3 method failed in the SCF and/or geometry convergency (supposedly, owing to a poor starting conformation). In such cases, the geometry optimizations were first performed at the AM1 level, and the resulting optimized, or at least par-
itially optimized structure was subjected to the subsequent PM3 treatment. However, the paper presents only the PM3 computed values.

The computations were primarily performed with the SPARTAN program package. However, for some limited amount of calculations the GAUSSIAN (G94) program was also applied. The geometry optimizations represent a central step in the computations. The optimizations were performed in Cartesian coordinates without symmetry constraints and with the first derivatives of energy constructed analytically. However, in some selected structural types the constrained coordinates were still applied to a limited degree in order to check the effects of imposed symmetry. In the geometry optima found, harmonic vibrational analysis was performed in order to check the geometrical nature of the optimized structures, and also to generate their IR vibrational spectra. In particular, the computed vibrational spectra were tested for presence of an imaginary frequency so that local minima and saddle points could be distinguished. This point is indeed relevant for nitro-derivatives of $C_{60}$ with respect to a relatively free internal rotation of the nitro groups.

The vibrational analysis was based on a numerical differentiation of the analytical energy gradient. The vibrational frequencies computed were not scaled down as the scaling factors for fullerenes are not well established yet. Moreover, the IR intensities require evaluation of the dipole-moment derivatives (actually, their squares). In fact, various quantum-chemical
packages handle the terms somewhat differently so that also the computed IR intensities differ (there is also a possible factor of SCF convergency difficulties during the numerical differentiation). All IR intensities reported here were derived by the GAUSSIAN program package. Moreover, the absolute IR intensities were converted into relative values in order to unify the simulated spectra (100% relative IR intensity scale). Relative stabilities of the structural isomers of C₆₀(NO₂)₂ were primarily evaluated by the relative heats of formation at room temperature ΔΔH°{sub}'. However, the HOMO-LUMO gaps have been considered as a possible alternative, too.

RESULTS AND DISCUSSION

Dinitro-derivatives represent a special case of C₆₀Z₂ fullerene derivatives. Although our computations represent the first comprehensive theoretical treatment of C₆₀(NO₂)₂, we can still use a nomenclature system introduced in other connections. Matsuzawa et al. enumerated altogether 23 positional isomers for a C₆₀Z₂ system, and also introduced a useful numbering system for the isomeric set. We have adopted the numbering system for the C₆₀(NO₂)₂ isomers, too (Fig. 1).

Addition of two nitro groups to the fullerene cage reduces its high symmetry considerably. In fact, the highest topological symmetry at all possible is C₂ᵥ. However, for the C₆₀(NO₂)₂ isomers we even cannot get this rela-
Fig. 1. The PM3 optimized structures of $C_{60}(NO_2)_2$. 
Fig. 1. (continuation) The PM3 optimized structures of \( C_{60}(\text{NO}_2)_2 \).
tively low symmetry. It turns out that the true local energy minima actually prefer a further symmetry reduction. This interesting fact is illustrated in Table 1 on several selected structures with a non-trivial topological symmetry. In order to evaluate the stabilization energy produced by the symmetry relaxation, we performed also partial geometry optimizations in which some symmetry constraints were imposed through a fixation of some torsion angles while bond distances and bond angles were still completely optimized. The results for this partial optimization are presented in the last column of Table 1, and the energies are always somewhat higher than for the related fully relaxed structures. In some cases, the stabilization energy is even close to about 3 kcal/mol. Hence, also with higher nitro-fullerenes we can well expect that their symmetries will be lower than the highest symmetry allowed simply by topology (before non-bonding interactions for the groups on the cage are considered).

Table 2 surveys structural and energy data for the all 23 computed isomers. The molecular structures are represented by their rotational constants $A$, $B$, and $C$. The inter-isomeric energetics is described by the relative heats of formation at room temperature $\Delta \Delta H_f^{298}$. It turns out that there are two low-energy structures while all the remaining species are separated by more than 10 kcal/mol from the computed ground state. In fact, the separation energies are sometimes considerably big. The species highest in energy are separated by more than 50 kcal/mol from the ground state. As nitro-
Table 1. Selected Relaxed and Symmetry-Constrained Structures\textsuperscript{a} of $\text{C}_{60}(\text{NO}_2)_2$

<table>
<thead>
<tr>
<th>Label\textsuperscript{a}</th>
<th>$\Delta H^\circ_{f,298}$\textsuperscript{b}</th>
<th>Symmetry</th>
<th>$\Delta H^\circ_{f,298}$\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mol</td>
<td>group</td>
<td>kcal/mol</td>
</tr>
<tr>
<td>7</td>
<td>787.362</td>
<td>$C_{2v}$</td>
<td>788.451</td>
</tr>
<tr>
<td>9</td>
<td>793.975</td>
<td>$C_{2v}$</td>
<td>796.122</td>
</tr>
<tr>
<td>15</td>
<td>808.268</td>
<td>$C_s$</td>
<td>808.424</td>
</tr>
<tr>
<td>2</td>
<td>809.533</td>
<td>$C_s$</td>
<td>812.230</td>
</tr>
<tr>
<td>13</td>
<td>815.928</td>
<td>$C_s$</td>
<td>816.986</td>
</tr>
<tr>
<td>16</td>
<td>816.872</td>
<td>$C_s$</td>
<td>817.602</td>
</tr>
<tr>
<td>56</td>
<td>818.966</td>
<td>$C_s$</td>
<td>819.491</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Fig. 1 for the numerical labels; table reports the PM3 heats of formation $\Delta H^\circ_{f,298}$.

\textsuperscript{b} Fully relaxed structure - the complete PM3 geometry optimization performed, resulting into $C_1$ symmetry.

\textsuperscript{c} The related symmetry-constrained structure; the symmetry constraints were imposed through torsion angles, however, there were no restrictions on the geometrical parameters still variable within the symmetry-constrained structure (i.e., a partial geometry optimization).
Table 2. The PM3 Computed Energies, HOMO-LUMO Gaps, and Structures\(^b\) of \(\text{C}_{60}(\text{NO}_2)_2\)

<table>
<thead>
<tr>
<th>Label(^b)</th>
<th>(\Delta H^\circ_{f,298})</th>
<th>(\Delta\Delta H^\circ_{f,298})</th>
<th>Gap</th>
<th>100(\times) A</th>
<th>100(\times) B</th>
<th>100(\times) C</th>
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<td>0.256</td>
<td>0.200</td>
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<tr>
<td>9</td>
<td>793.975</td>
<td>6.613</td>
<td>6.428</td>
<td>0.267</td>
<td>0.194</td>
<td>0.189</td>
</tr>
<tr>
<td>23</td>
<td>798.915</td>
<td>11.553</td>
<td>5.945</td>
<td>0.224</td>
<td>0.221</td>
<td>0.187</td>
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<tr>
<td>15</td>
<td>808.268</td>
<td>20.906</td>
<td>5.466</td>
<td>0.245</td>
<td>0.207</td>
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<tr>
<td>41</td>
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<td>5.533</td>
<td>0.245</td>
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<td>0.266</td>
<td>0.194</td>
<td>0.188</td>
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<tr>
<td>24</td>
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<td>5.027</td>
<td>0.228</td>
<td>0.219</td>
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<tr>
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<tr>
<td>57</td>
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<td>4.720</td>
<td>0.233</td>
<td>0.212</td>
<td>0.185</td>
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<tr>
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<td>4.720</td>
<td>0.234</td>
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<td>0.236</td>
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<tr>
<td>35</td>
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<td>4.614</td>
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<tr>
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<td>4.496</td>
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<td>0.185</td>
<td>0.184</td>
</tr>
<tr>
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<td>829.579</td>
<td>42.217</td>
<td>4.813</td>
<td>0.261</td>
<td>0.196</td>
<td>0.189</td>
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<tr>
<td>6</td>
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<td>43.716</td>
<td>4.516</td>
<td>0.260</td>
<td>0.198</td>
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<tr>
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<td>833.734</td>
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<tr>
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<td>3.841</td>
<td>0.258</td>
<td>0.193</td>
<td>0.184</td>
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<tr>
<td>33</td>
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<td>50.735</td>
<td>3.130</td>
<td>0.229</td>
<td>0.216</td>
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<tr>
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<td>52.869</td>
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<td>0.262</td>
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<td>2.910</td>
<td>0.277</td>
<td>0.183</td>
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</tbody>
</table>

\(^a\) Rotational constants \(A, B, C\) in \(\text{cm}^{-1}\), multiplied by 100 for graphical brevity.

\(^b\) See Fig. 1 for the numerical labels.
fullerenes, in contrast to the pristine fullerenes, are prepared at moderate temperatures, entropy effects should not influence the inter-isomeric relative stabilities substantially.

In the ground state the two nitro groups are placed in para position on one hexagon (structure coded 7 - see Fig. 1). The next structure is higher in the PM3 energy by more than 6 kcal/mol (Table 2) and it is produced by the addition to one 6/6 (double) bond of the cage (structure coded 9 in Fig. 1). The third lowest structure is already almost 12 kcal/mol above the system ground state (structure coded 23 in Fig. 1). Table 2 also reports the PM3 computed HOMO-LUMO gaps as an alternative stability measure. It is interesting to note that in this system the computed HOMO-LUMO gaps essentially correlate with the stability order deduced from the heats of formation. However, there is an exception with the structure coded by 9 which actually exhibits the biggest HOMO-LUMO gap though it is not the ground state. There are some other minor irregularities in the order by the HOMO-LUMO gaps compared to the energy order.

Cataldo observed the FT-IR spectra of $C_{60}(NO_2)_4$ and reported a particularly strong band at 1570 cm$^{-1}$ (asymmetric NO$_2$ group stretching). Although we compute only dinitro-derivatives, the feature should not be changed substantially. Fig. 2 presents the PM3 computed IR spectra for the three isomers lowest in energy (7, 9, 23) and indeed, a particularly strong line is present around 1580 cm$^{-1}$ in all the three isomers of $C_{60}(NO_2)_2$. How-
ever, there are also some differences between the computed spectra so that the IR spectra, once recorded also for C\textsubscript{60}(NO\textsubscript{2})\textsubscript{2}, could help in structure elucidation. Other interesting features are some cage related lines, enhanced by a suppression of the symmetry selection rules through derivatization.

In conclusion, the PM3 computations of dinitro-derivatives of C\textsubscript{60} reveal that low-energy structures have either the two nitro groups placed in para position on one hexagon, or added to one 6/6 (double) bond of the cage. The optimized structures tend to have $C\textsubscript{1}$ symmetry. In other words, they do not follow a higher symmetry, if allowed by topology, as their symmetry is lowered due to non-bonding interactions. The suggested structural rules should help in computations of tetranitro- and hexanitro-derivatives as the number of all possible structural isomers increases rapidly\textsuperscript{36} and some structural pre-selection is thus essential.

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**Fig. 2.** The PM3 IR spectra of C\textsubscript{60}(NO\textsubscript{2})\textsubscript{2}: 7 (bottom), 9, and 23 (top).
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