Predicted Phototoxicities of Carbon Nano-material by Quantum Mechanical Calculations

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SCIENCE

Abstract

The purpose of this research is to develop a predictive model for the phototoxicity potential of carbon nanomaterials (fullerenols and carbon single-walled nanotubes). This model is based on the quantum mechanical (*ab initio*) calculations on these carbon-based materials which allow the comparison of the triple excited states of the materials to published work relating phototoxicity of polynuclear aromatic hydrocarbons (PAH) to their predictive triple states.

Background

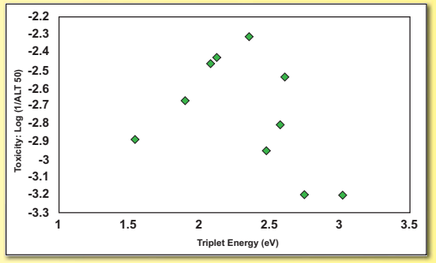
Several authors studied the connection between toxicity and the excited states of the subject molecule (Newsted, J.L., Giesy, J.P., 1987. Environ. Toxicol. Chem. 6, 445; Mekenyan, O.G., Ankley, G.T., Veith, G.D., Call, D.J., 1994. Chemosphere 28, 567).

The triplet excited state energy of the molecule was found to play an important role in predicting median lethal time (LT50) for polynuclear aromatic hydrocarbons.

The number of photons hitting the earth plays a role in phototoxicity, because various wavelength regions in natural sunlight have different number of photons. The higher energy photons are absorbed by the atmosphere before they reach the surface. If all wavelengths had similar number of photons, the phototoxicity curve would be linear increasing with the energy of the photons (or decreasing with the increasing wavelength of the photons) Because of this uneven distribution of photons, the phototoxicity curve shows a parabolic relationship.

This study will use the model from Betowski, L. D., Enlow, M., Riddick, L, 2002. Computers & Chemistry, 26(4),371-377, which is shown on the next figure. The toxicities and calculated triplet states are for polynuclear aromatic hydrocarbons.

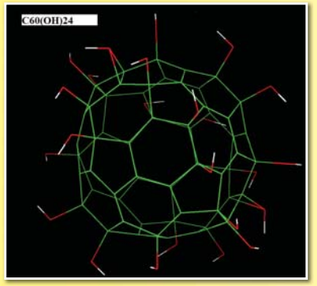
Photo toxicity of PAHs as a function of their triplet excited states; phototoxic range 1.5 to 2.5 eV



Methods

The toxicities of the PAHs used are those reported by Newsted and Giesy.

Calculations on the fullerenols and carbon nanotubes were performed using the Gaussian 09 programs (Gaussian 09, Revision A.02, M. J. Frisch et al.). Complete geometry optimizations for the neutral forms of all molecules were first carried out using *ab initio* calculations at two levels of theory, followed by frequency calculations in order to verify that the stationary points thus obtained were true minima. Triplet excited state calculations were performed using the configuration interaction approach.

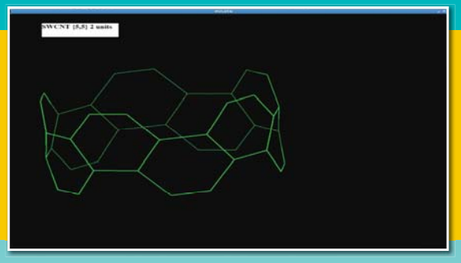


Geometry optimization @ Hartree-Fock level with a 6-311G(d,p) basis set (wavefunction approximation)

Fullerenols	Triplet Energy (eV) (RCIS/6-311G(d,p)) (symmetry)
$C_{60}(OH)_4$	1.8808 (D2h)
$C_{60}(OH)_8$	1.8340 (D2h)
$C_{60}(OH)_{12}$	1.6944 (C2h) 1.6947 (Cl)
$C_{60}(OH)_{16}$	1.6998 (Cl) 1.7715 (D2)
$C_{60}(OH)_{20}$	1.6930 (D2)
$C_{60}(OH)_{24}$	2.0345 (C2) 1.0334 (C2)

Carbon Nanotubes

There are many variations of carbon nanotubes, both single walled and double walled. The single-walled nanotubes are characterized by their chiral indices {m,n}. There are three kinds of structures: 1) n=0, the so-called zigzag structures; 2) n=m, the armchair structures; and 3) the rest, called the chiral structures. The other dimension for these nanotubes is the number of translational unit cells.



Single walled carbon nanotubes
Geometry optimization @ HF/6-311G(d,p)

SWCNT	Triplet Energy (eV) (RCIS/6-311G(d,p))
{5,5} 2 units	1.3804 eV
{10,10} 2 units	1.4136 eV

Discussion

From the figure the phototoxicity range runs from approximately 1.5 eV to 2.5 eV increasing linearly to 2.4 eV. The curve drops off precipitously after 2.6 eV. From the tables most of the fullerenols fall into the moderately toxic range.

Roberts, J.E., Wielgus, A.R., Boyes, W.K., Andley, U., Chignell, C.F. (Toxicology and Applied Pharmacology 228 (2008) 49–58) found the acute toxicity of water-soluble nano-$C60(OH)_{22-26}$ is low, but these compounds are retained in the body for long periods, raising concern for their chronic toxic effect.

Our calculated results agree with the results found in the above study in that the fullerenols have toxicity but it is low.

The SWCNT appear to be just below the toxicity region. However, these compounds were just modeled with two units, while in reality they exist as many units.