Fall 2010

Solvent Effects on Emission Spectra of Carminic Acid and Determination of its Ground and Excited State Dipole Moments

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ABSTRACT:

Absorption and fluorescence emission spectra of Carminic acid were recorded in solvents with different solvent parameters like polarities, dielectric constant and refractive index. The solvents used in the experiment were water, DMSO, acetonitrile, methanol, propanol and butanol. The atomic radius of the molecule was found out using Hartree-Fock method in molecular modeling using Spartan software and it is applied to find out the dipole moments. The dipole moments of Carminic acid in the ground state and excited states have been determined and Solvatochromic shift method has been used to determine the excited state dipole moments. The linear progressions were made and the slopes were determined from absorbance and fluorescence band shifts. The conclusions on the spectral shifts were done based on the polarity function of the solvents and the dipole moments in ground and excited states of the molecule.

INTRODUCTION:

Carminic acid is a red glucosidal hydroxyanthrapurin with a chemical formula $C_{22}H_{20}O_{13}$.

The chemical structure as given in (Fig. 3.) has a core anthraquinone structure (Fig. 1.) linked to a glucose sugar unit (Fig. 2.)

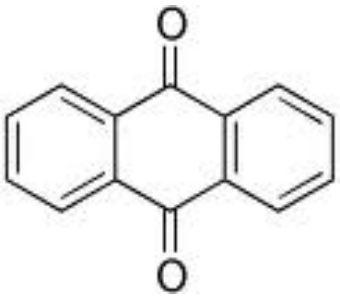


Fig. 1. Core Anthaquinone structure.

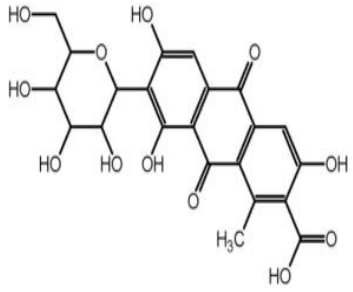


Fig. 2. Glucose Sugar Unit

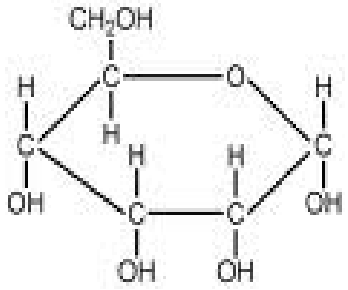


Fig. 3. Chemical Structure of Carminic Acid.

Properties

Carminic acid is light and heat stable it is available in three forms. They are Cochineal extract, Carmine, Carminic acid.

Side effects: Anaphylactic shock and allergy

Preparation of Carminic acid and Carmine from Cochineal insects

Cochineal bugs are scientifically called as Dactylopius Coccus and they live and grow on cactuses. They are biologically classified into male and female. Males stop feeding when matured and die after mating. Female produces nymphs. Nymphs produce red pigment called Carminic acid for protection. Two kinds of farming the bugs are done. One is Natural farming called as Nopalry. The other one is Artificial farming in which the bugs are allowed to grow in zapotec nests. The cactuses are grown in farms and are injected with these cochineal bugs and they are allowed to develop and grow and after 90 days, they are harvested. Then, they are sent for processing into food colorant and dye. They kill the bugs by putting them into hot water or dry them in sunlight or an oven. These, different procedures produce different intensity of color. 60,000-70,000 female insects produce 1 lb of Carminic acid, which costs 50-75$ (olden days more than gold price). 2 principal forms of dye are present with different preparations. One, to grind the dried bugs into a powder called as cochineal extract. Second, to chemically remove the dye from bug called as carmine. To prepare carmine, the powdered insect bodies are boiled in ammonia or a sodium carbonate solution, the insoluble matter is removed by filtering, and alum is added to the clear salt solution of Carminic acid to precipitate the red aluminium salt. Purity of color is ensured by the absence of iron. For shades of purple, lime is added to the alum.

Uses of Carminic acid:

Carminic acid is available in two forms, water soluble and water insoluble form. Water soluble form is used in foods like sausages, red meat, jams, jellies, icing, toppings, dairy products, red marinades, drinks Coca Cola.

Water insoluble form is used in liquids like beverages.

It is used in dyeing wool fabrics because Carminic acid has a very good affinity with wool rather than other fabric like silk. It became a very good export item for the European industry. Carminic acid was used in the early oil paintings during the colonial period.
Only Carminic acid is used in the cosmetics in the eye area, because of its non-toxic nature and anti-carcinogenic properties. It is also used in cosmetics like lipsticks, eyeshades and nail lacquers.
It is used in medical field for treating seizures, epilepsy, diabetic neuropathies and warts.
It is used in the micro biology department as a stain and in pharmaceutical Industry to color pills and capsules.

Experimental procedure:

We picked 6 different solvents with different solvent parameters like refractive index, dielectric constant and mainly polarities. They are water, Acetonitrile, Methanol, Propanol, Butanol and DMSO.
Carminic acid was purchased from Sigma Aldrich Company with a lot number MKBB8217.
The absorption spectra in different solvents were recorded from Ocean Optics USB 4000 spectrometer using Logger Pro software.
The fluorescence spectra in different solvents were recorded from Varian fluorometer, NIU (Northern Illinois University).
The atomic radius was found out by making a 3D structure of the molecule using Spartan software and Chemdraw software.
The Di electric constant, refractive index, polarities of all the solvents and the absorption and emission wavelengths of Carminic acid in their respective solvents are given in the following table:

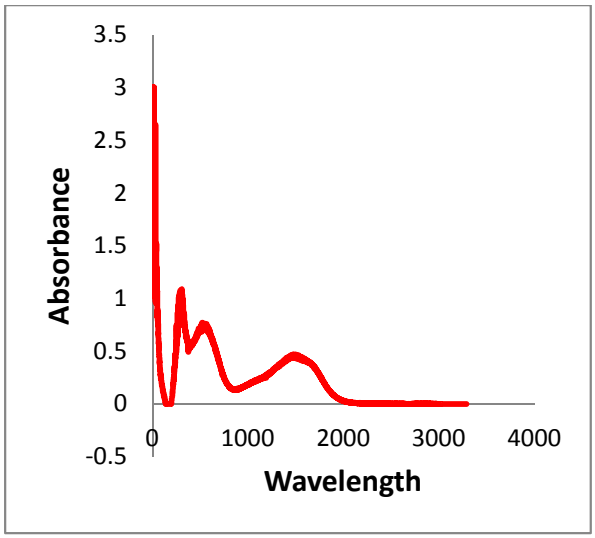
Solvent	λabs	λem	Εb	ηb	P'
Water	226.5	431	80	1.333	10.2
DMSO	290.5	538	48	1.479	7.2
Acetonitrile	220.3	572	38.8	1.344	5.8
Methanol	279.3	579	32.7	1.328	5.1
Propanol	223.7	406	20.3	1.385	4
Butanol	220.3	585	17.1	1.397	3.9

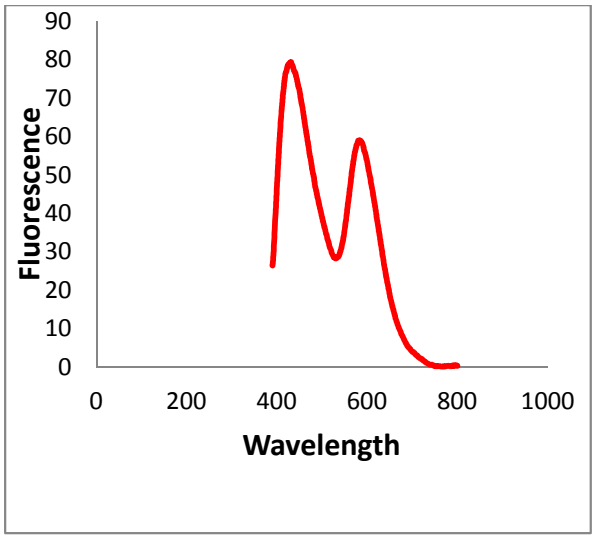
Absorbance and Florescence spectra's of Carminic acid in all the solvents are shown below.

WATER

Absorption in *Water*

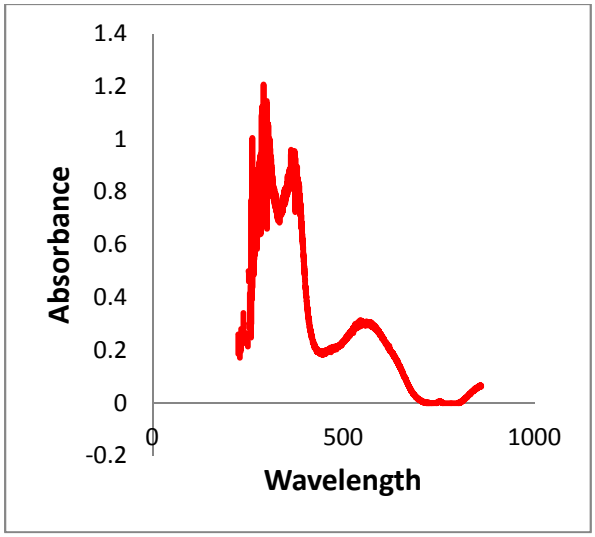
Fluorescence in *Water*



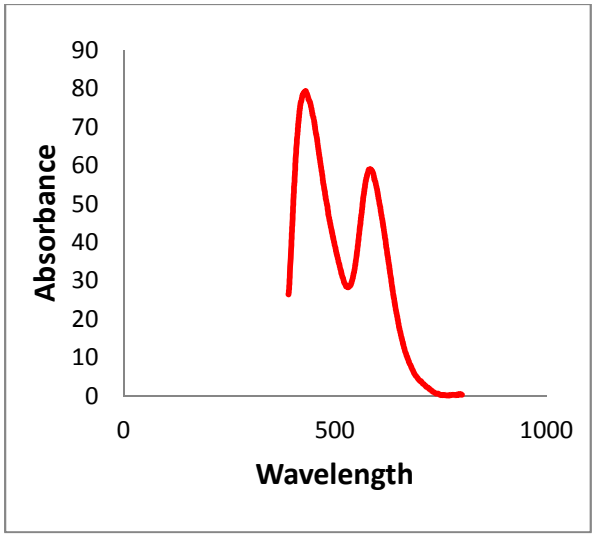


Dimethyl Sulfoxide

Absorption in *Dimethyl Sulfoxide*



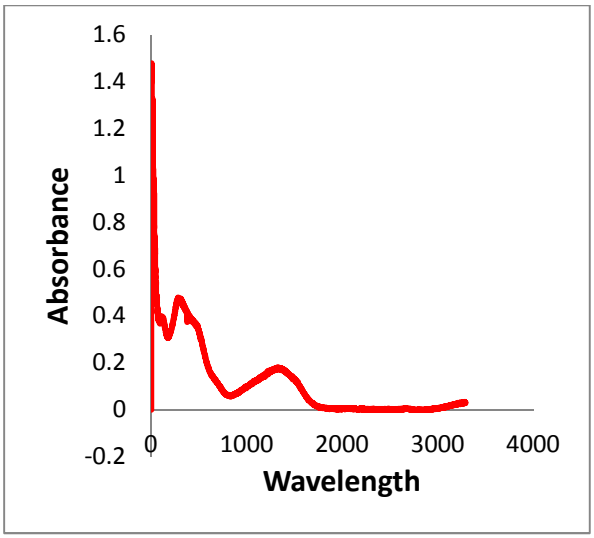
Fluorescence in *Dimethyl Sulfoxide*

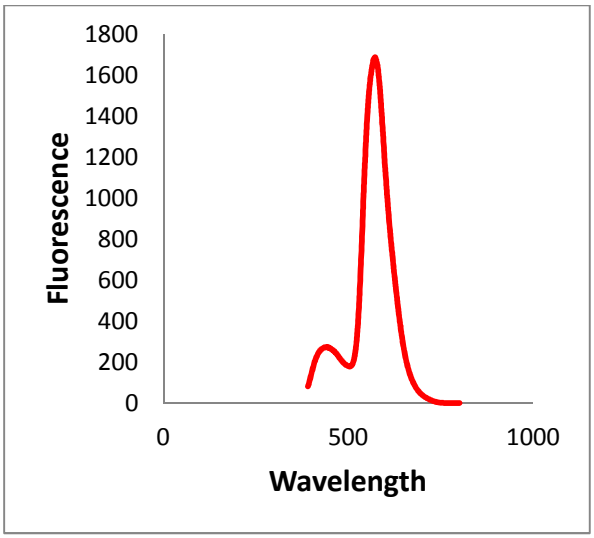


Acetonitrile

Absorption in *Acetonitrile*

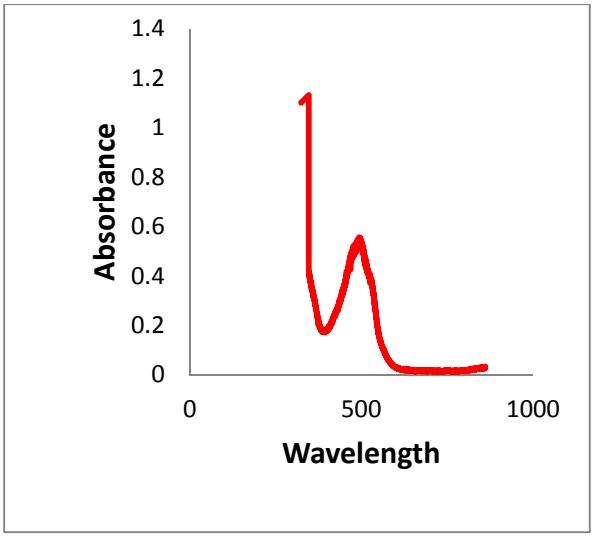
Fluorescence in *Acetonitrile*



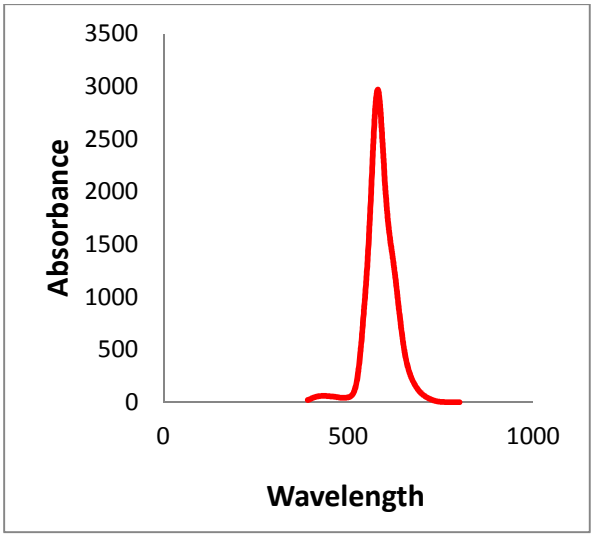


Methanol

Absorption in *Methanol*



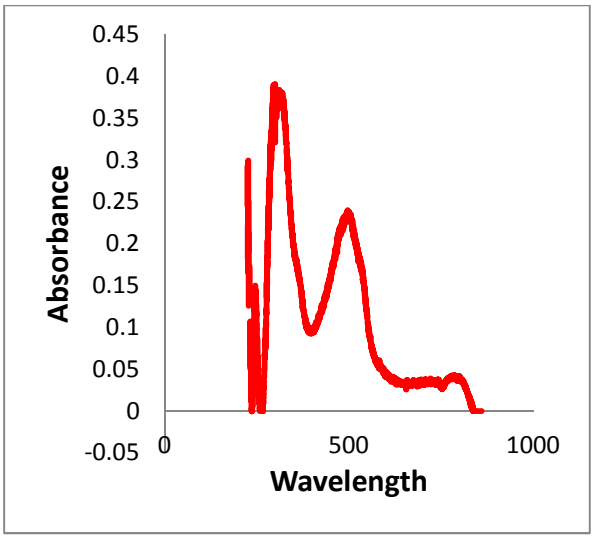
Fluorescence in *Methanol*

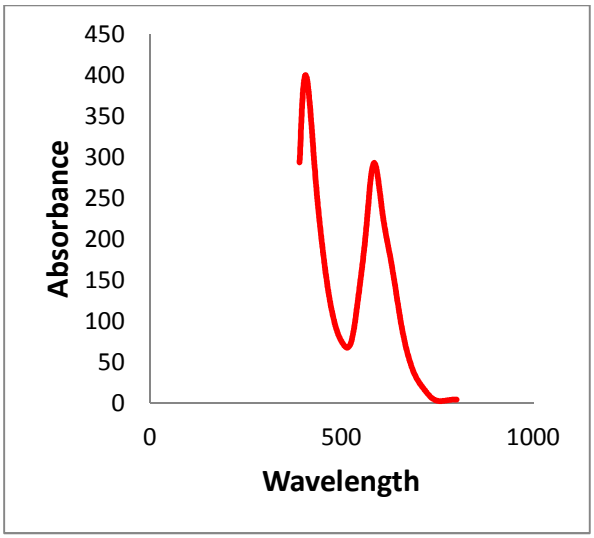


Propanol

Absorption in *Propanol*

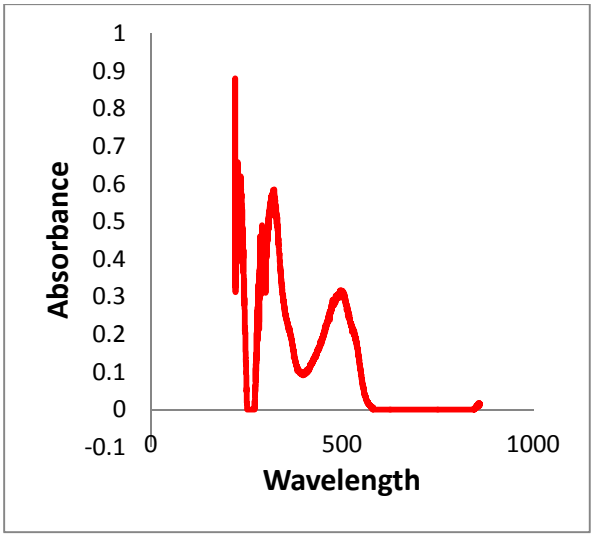
Fluorescence in *Propanol*



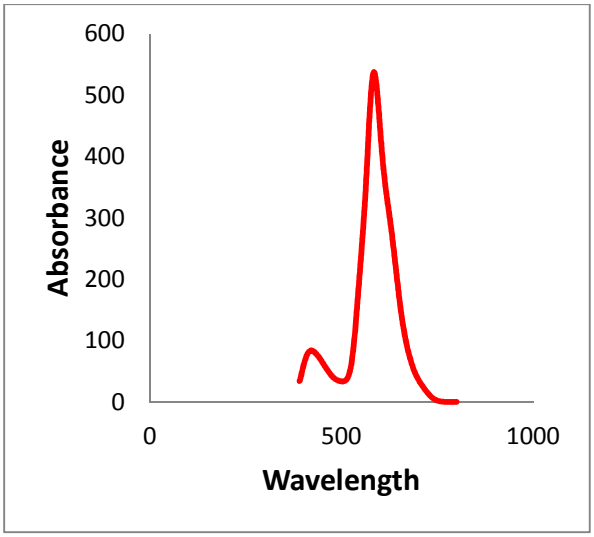


Butanol

Absorption in *Butanol*



Fluorescence in *Butanol*



Equations:

The equations involved in this project are shown below:

$$\bar{\upsilon}_a - \bar{\upsilon}_f = m_1 f(\varepsilon, \eta) + \ const$$

$$\bar{\upsilon}_a + \bar{\upsilon}_f = -m_2[f(\varepsilon, \eta) + 2g(\eta)] + const$$

$$f(\varepsilon, \eta) = \frac{2n^2+1}{n^2+1}\left[\left(\frac{\varepsilon-1}{\varepsilon+1}\right) - \left(\frac{2n^2-1}{n^2+1}\right)\right]$$

$$g(\eta) = \frac{3}{2}\left[\frac{(n^4-1)}{(n^2+2)^2}\right]$$

$$m_1 = \frac{2(\mu_e-\mu_g)^2}{hca^3}$$

$$m_2 = \frac{2(\mu_e{}^2-\mu_g{}^2)^2}{hca^3}$$

$$\mu_e = \frac{(m_1+m_2)}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}}$$

$$\mu_g = \frac{(m_2-m_1)}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}}$$

Here, $\bar{\upsilon}_a - \bar{\upsilon}_f$ and $\bar{\upsilon}_a + \bar{\upsilon}_f$ are the differences in the spectral shifts of absorption and emission maxima. ε, η are the dielectric constant and refractive index values. $f(\varepsilon, \eta)$ and $g(\eta)$ are the functions. $m_1 and\ m_2$ are the slopes of the equations. μ_e and μ_g are the dipole moments of Carminic acid in ground state and excited state respectively.

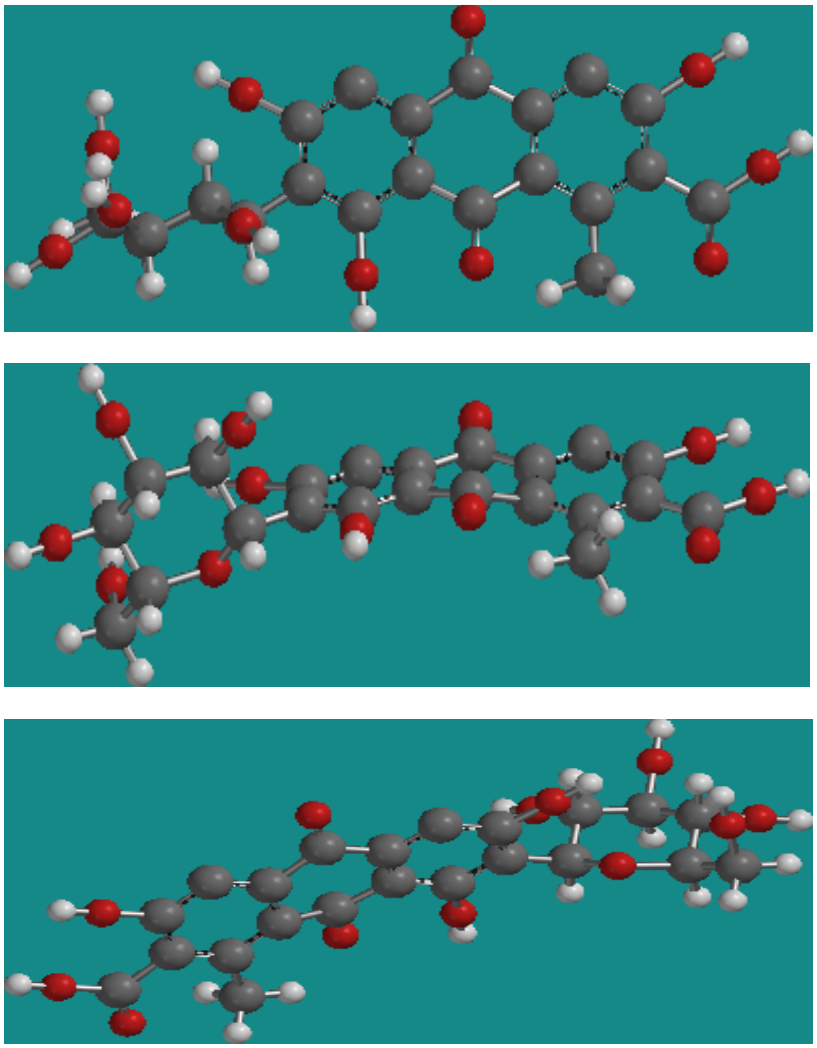
Where, "a" is atomic radius of the drug molecule obtained from the 3D image of the drug molecule.

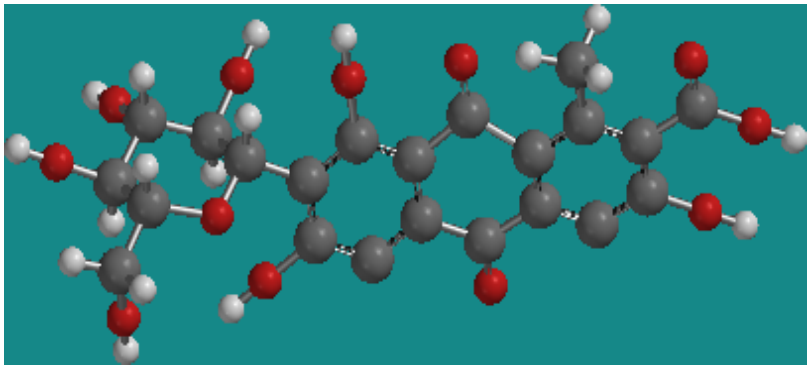
Spartan software was used to draw the molecule.

The longest distance between any two atoms of the drug molecule is taken as the radius.

The method used for finding the radius is called as Hartree-Fock method.

The atomic radius of the developed 3D structure was found to be 16.285 Angstroms.





Different views of the 3D structure of Carminic acid

Results and Discussions:

Firstly, the absorption and emission maxima wavelengths are measured and recorded. The atomic radius is taken from the drawn 3D structure of the drug molecule. The spectral shifts are calculated. Dielectric constant and refractive index values of all the solvents are taken and then finally all the values are substituted in the respective equations and the dipole moments of Carminic acid are calculated in all the solvents in ground state and in excited state. The calculated values are shown in the table given below.

Calculations and values

Solvent	Λ_{abs}	λ_{em}	$\bar{\upsilon}_a$	$\bar{\upsilon}_f$	$\bar{\upsilon}_a - \bar{\upsilon}_f$	$\bar{\upsilon}_a + \bar{\upsilon}_f$	$f(\varepsilon,\eta)$	$g(\eta)$	$f(\varepsilon,\eta) + 2g(\eta)$
Water	226.5	431	44150.11	23201.86	20948.25	67351.97	0.913579	0.226851	1.367272
DMSO	290.5	538	34423.41	18587.36	15836.05	53010.77	0.842573	0.323779	1.490130
Acetonitrile	220.3	572	45392.65	17482.52	27910.13	62875.16	0.866018	0.234279	1.334575
Methanol	279.3	579	35803.80	17271.16	18532.64	53074.95	0.854841	0.223469	1.301779
Propanol	223.7	406	44702.73	24630.54	20072.18	69333.27	0.779026	0.261806	1.302639
Butanol	220.3	585	45392.65	17094.02	28298.63	62486.66	0.747115	0.269812	1.286739

Slopes and Dipole moments

Solvent	$m_1 = \frac{\bar{\upsilon}_a - \bar{\upsilon}_f}{f(\varepsilon,\eta)}$	$m_2 = \frac{\bar{\upsilon}_a + \bar{\upsilon}_f}{f(\varepsilon,\eta) + 2g(\eta)}$	$\mu_g = \frac{(m_2 - m_1)}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}}$	$\mu_e = \frac{(m_1 + m_2)}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}}$	$\mu_e = \frac{(m_1 + m_2)}{(m_2 - m_1)}(\mu_g)$
Water	22929.88821	59058.42936	8.7359E-25	1.98248E-24	1.98248E-24
DMSO	18794.87566	45450.09373	7.11902E-25	1.71584E-24	1.71584E-24
Acetonitrile	32228.12759	57143.84433	5.08176E-25	1.82281E-24	1.82281E-24
Methanol	21679.64071	49220.50608	6.84872E-25	1.76311E-24	1.76311E-24
Propanol	25765.75386	66613.30056	9.31757E-25	2.10722E-24	2.10722E-24
Butanol	37877.18851	61446.5572	4.43422E-25	1.86863E-24	1.86863E-24

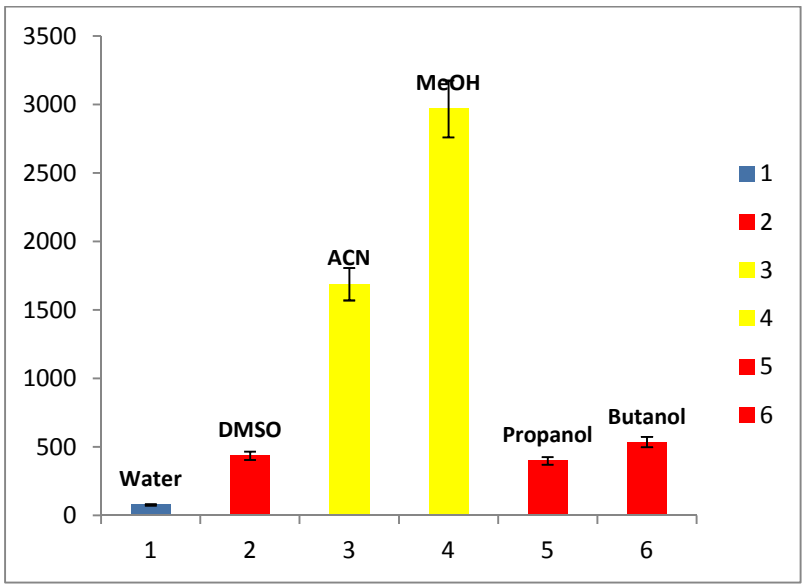
Results: From the obtained results, the dipole moments in the excited state of Carminic acid were greater than the dipole moments in the ground state. From this, we can conclude that the Carminic acid is more Polar in the excited state then in ground state.

The maxima wavelengths of absorption and fluorescence of Carminic acid in all the solvents were recorded and compared. The comparison tables and graphs are shown below:

Comparison of Fluorescence

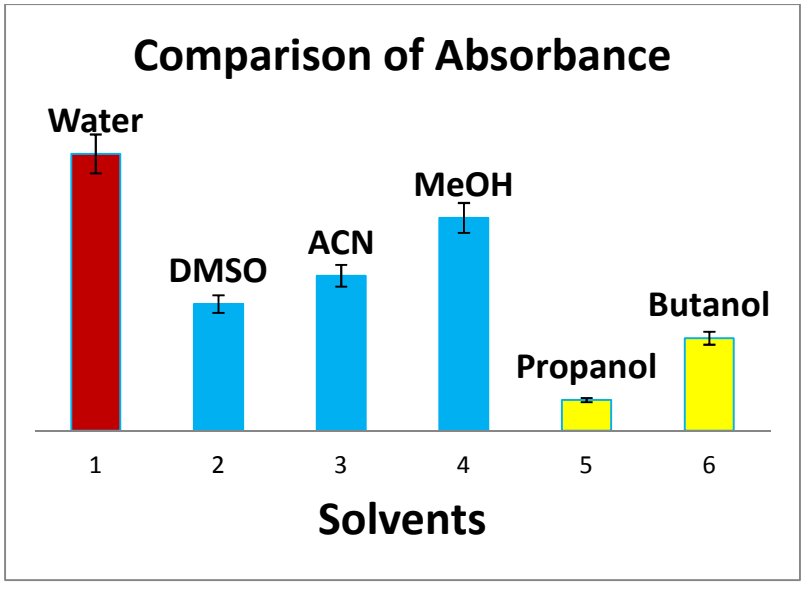
Solvent	Wavelength	Frequency
Water	431	79.38
DMSO	538	436.7
Acetonitrile	572	1689
Methanol	579	2969
Propanol	406	400.5
Butanol	585	537.1

Here, we observe that the fluorescence wavelengths of Carminic acid in all the solvents follow a very good pattern i.e. in an increasing order except that of Propanol. This might be because we used iso-propanol instead of n-propanol.



Comparison of absorbance

Solvents	Wavelength	Intensity
Water	226.5	2.639
DMSO	290.5	1.207
Acetonitrile	220.3	1.477
Methanol	279.3	2.029
Propanol	223.7	0.292
Butanol	220.3	0.881



Here, the absorption wavelengths follow a decreasing order except that of methanol. This is because of the strong hydrogen bonding in Methanol.

Conclusions:

The absorption and emission wavelengths of Carminic acid in different solvents are measured and recorded. The atomic radius of the drug molecule has been derived from the 3D structure of the molecule. The comparison tables and graphs were made for the absorption and fluorescence wavelengths. Final derivations of dipole moments of Carminic acid in ground state and excited state were made using the solvatochromic shift method. The dipole moments of Carminic acid in excited state were greater than in ground state. From this, we can conclude that Carminic acid is more Polar in excited state than in ground state. Thus, makes Carminic acid an important drug used as a laser gain.

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