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# **ORIGINAL STUDY**

# Studying Some Physical Properties of Rhodamine Dye(6G) and Showing the Effect of Carbon on HOMO-LUMO

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#### Abstract

In this research, some important physical properties of Rhodamine 6G dye, a type of Xanthine dye, whose emission is located between  $(0.5-0.7) \mu m$ . Were studied double bond [C=C], [C=H] and [C=N], addition singular for the bonds [C-C], [C-N], [C-H] and [C-O], the calculation of the constants of forces. Here, too, the double bond was the largest value than the singular, the same thing applies when the value of the heat of formation for each bond was calculated and two programs were used, the first for drawing and the second for the calculations, which are (CS Chem Draw 5.0 Manual, CS Chem Office Pro 2000) respectively, and when calculating the vibrational patterns of the bonds, the double bond was the least patterned. Calculation of the streatching vibration patterns, bendening vibration patterns, and streatching - bendening patterns of the dye, and finally the calculation of the HOMO –LUMO forms and the drawing of their shapes.

*Keywords:* Rhodamine 6G, Dye, Xanthine dye, Double bond, Single bond, HOMO–LUMO, Heat of formation, Laser dye, 7-Hydroxycoumarin, Fluorescence

# 1. Introduction

• he typical laser medium is a dye that is optically pumped by a flashlamp or a beam from another laser. The dye is typically toxic but occasionally edible and is dissolved in a solvent such water, alcohol, or ethylene glycol (antifreeze) at a concentration of  $10^{-4}$  M. The dye is often made up of hydrocarbons and other atoms joined in a convoluted chain with at least 50 atoms. Table (1) displays a short selection of the dyes' molecular structures, their tuning range, and some of their solvents. Fig. (1). Demonstrates different colors' tuning ranges when pumped by various common sources. It is clear that there is a complex interaction between the dye concentration, solvent, and pump wavelength that influences the tuning range and efficiency. Another factor is the dye's chemical lifetime. One looks for a straightforward approximation model that matches the experimental results because there are so many potential couplings

between complex atom configurations. The straightforward chemical model displayed in Fig. (2) is likely the most effective. The classical motion of the vibrations corresponding to the energy levels in both the ground and excited states is assumed to be described by some interaction potential based upon a molecular coordinate (q) (a distance). The fact that the minimum of the potential for the first excited state is moved along this coordinate axis relative to the minimum of the ground state is the most important problem with this sketch. The likelihood that the "molecules" in each manifold will occupy their positions is given by the Boltzmann factor, exp [-(E-E<sub>min</sub>)/kT]. The optical absorption travels vertically to a high vibrational state of S<sub>1</sub> from the densely inhabited area close to  $(q_0)$ in S<sub>0</sub>.

The occupation probability of the states in  $S_1$  is likewise characterized by the Boltzmann factor with reference to the lowest state in  $S_1$  while the molecule is in  $S_1$ , as the surplus energy,  $E_2$ , is quickly distributed across the complex molecule's

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Dye	Structure	Solvent	Wavelength	
Acridine red	(H <sub>3</sub> C)NH	EtOH	Red 600–630 nm	
Puronin B	$\dot{H}$ $(C_2H_3)_2N$ $\dot{N}H(C_2H_3)_2$ CF	MeOH H <sub>2</sub> O	Yellow	
Rhodamine 6G	$\begin{array}{c} H\\ C_2H_3HN\\ H_3C\\ \end{array}$	EtOH MeOH H20 DMSO Polymethy-lmethacrylate	Yellow (570–610) nm	
Rhodamine B	(C <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> N	EtOH MeOH Polymethy-lmethacrylate	Red 605—635 nm	
Na-fluorescein	NaO O O O COONa	EtOH H <sub>2</sub> O	Green 530–560 nm	
2,7-Dichlorofluorescein	HO CI CI CI	EtOH	Green 530–560 nm	
7-Hydroxycoumarin	O O OH	H <sub>2</sub> O (pH ~ 9)	Blue 450–470 nm	
4-Methylembelliferone	ОСОСОН	H <sub>2</sub> O (pH ~ 9)	Blue 450—470 nm	
Esculin	CH <sub>3</sub> O H OH H H HC - C - C - C - C - C + OH O O O O O O O O	H <sub>2</sub> O (pH ~ 9)	Blue 450—470 nm	

Table 1. Molecular structure, laser wavelength, and solvents for some laser dyes [1].



Fig. 1. Performance of various dyes when pumped with an argon-ion or Krypton-ion laser [1].



Distance

Fig. 2. Energy-level diagram typical of a dye [2].

numerous vibrational modes. As a result, the majority of the atoms in S1 are located at  $E_1$  with a coordinate ( $q_1$ ) that is displaced relative to ( $q_0$ ). The lower state of the emitted photons is a highly excited one in the ground manifold since the  $S_1 \rightarrow S_0$  emission is likewise vertical. Thus, the following kinetic sequence can be used to signify lasing or fluorescence [1]:

# 1.1. Dye lasers

Organic dyes dissolved in ethyl, methyl alcohol, glycerol, or water serve as the laser gain medium. These dyes can be activated optically, such as with argon lasers, and emit light at a variety of wavelengths, including 390–435 nm (stilbene), 460–515 nm (coumarin 102), 570–640 nm (rhodamine 6G), and many others. Due to their broad tuning ranges, these lasers have been extensively used in research and spectroscopy. Since dyes are cancercausing, dye lasers went extinct as soon as tunable solid state laser medium were made available [3].

#### 1.1.1. Xanthene dyes

Xanthene dyes are often quite effective and cover the 500–700 nm range in wavelength. The majority of dye lasers used in industry fall into this category; the two most used laser dyes are fluorescein and rhodamine B. The two identical mesomeric structures shown in Fig. (3) can be used to illustrate the electron distribution in the chromophore in xanthenes dyes.

#### 1.1.2. Rhodamine 6G

Fig. (4) depicts effective laser action in the 590 nm range and typically flashlamp-pumped dye lasers have lases with an efficiency of around 1 %. It serves



Fig. 3. Two identical mesomeric structures (A) and (B) [4].



Fig. 4. Structures of Rhodamine 6G [4].

as a standard dye against which the efficacy of other dyes is evaluated. This laser dye, Rhodamine 6G, is one of the most utilized and researched due to its strong photostabilty. In the 560–800 nm range, the majority of xanthene laser dyes exhibit effective laser activity. Another successful molecularly engineered laser dye is rhodamine 700, shown in Fig. 5. This effective dye operates as a laser between 700 and 800 nm.

#### 1.1.3. Rhodamine 700

Features a "double butterfly" shape that, as seen in Fig. 4, makes the amino groups more stiff and planar. Rhodamine 6G's photostability is improved by substituting a -CF3 group for the phenyl group.

# 1.2. Jablonski diagram

The Jablonski diagram, named for Polish physicist Aleksander Jablonski, can be used to clarify fundamental concepts in molecular photophysics (Fig. 6).

Solid arrows in Fig. (6) denote radiative transitions that happen as a result of a photon's absorption (violet, blue) or emission (green for fluorescence; red for phosphorescence). Non-radiative transitions (violet, blue, green, and red) are represented by dashed arrows. When a vibrational state from a higher electronic state is coupled to a vibrational



Fig. 5. Structures of Rhodamine 700 [4].



Fig. 6. Jablonski diagram representing energy levels and spectra.

state from a lower electronic state, internal conversion, a non-radiative transition, takes place. The first subscript in the notation of, for instance, S1,0 denotes the electronic state (first excited), and the second one the vibrational sublevel (v = 0). The graphic shows the following internal conversions:

 arrow from  $S_{1,0} \rightarrow T_{1,0}$ , is a non-radiative transition between states with varying spin multiplicities. Sketches of the absorption, fluorescence, and phosphorescence spectra are displayed below the diagram. The diagram shows a molecule's electronic states and how they change over time. By energy, the electronic states are organized vertically. By spin multiplicity, they are arranged horizontally. The singlet ground state (S<sub>0</sub>) and two higher singlet excited states (S<sub>1</sub> and S<sub>2</sub>) are shown in the left portion of the diagram as three singlet states with anti-parallel spins. Due to the fact that they do not interact with an outside magnetic field, singlet states are diamagnetic. The electronic state with parallel spins is known as the triplet state (T<sub>1</sub>). An external magnetic field interacts with a molecule that is in the triplet state. It is possible to change between electronic states with the same spin multiplicity. Despite being technically forbidden, transitions between states with differing spin multiplicities can happen due to a phenomenon known as spin-orbit coupling. Intersystem crossing is the term for this transition. The vibrational states, which have significantly lower energy than these electrical states, are superimposed on them. We shall discuss the series of events that take place when an aromatic molecule absorbs a photon with enough energy in the sections that follow [5].

### 1.3. Fluorescence

The term "fluorescence" was first used by British scientist Sir George G. Stokes in 1852 when he noticed blue luminescence in the mineral fluorite. Stokes also made the discovery of the redshift, or Stokes-shift, between the band maximum of the fluorescence spectrum and the band maximum of absorption. The fluorescence emission to the ground state  $S_{0}$ , internal conversion to  $S_{0}$ , and intersystem crossing to the lowest triplet state all begin at the lowest vibrational level of  $S_1$  (Fig. 6).

Depending on the chemical species, fluorescence can last anywhere between one and one hundred nanoseconds on the nanosecond timescale  $(1ns = 10^{-9} \text{ s})$ . The Jablonski figure makes it obvious that no matter what electronic energy level is triggered, fluorescence always starts at the same level. The emission state is the first excited state  $S_{1,0}$ 's zeroth vibrational level. This results in a Stokes shift, where the fluorescence spectra is shifted to a lower energy than the matching absorption spectrum. Solvent interactions have the potential to increase the Stokes shift.

We may also infer from the rough sketches of the spectra in Fig. 6 that vibronic bands in an absorption spectrum provide information on vibrations in higher electronic-excited states while vibrational fine structure in a fluorescence spectrum reports on vibrations in the ground state.

The Franck-Condon factor is an additional element that must be taken into account in fluorescence spectroscopy. The fluorescence transition  $S1,0 \rightarrow S0,0$ is not the strongest one, as can be seen in Fig. 6's Jablonski scheme. According to the Franck-Condon principle, the transition between the vibrational state in the ground state and that state in the excited state is the most intense (see Fig. 7, blue arrow).

#### 1.4. Phosphorescence

The triplet state is also seen in Fig. 6. The molecule will stay in this form for a very long time (between microseconds and seconds) before decaying back to the ground state. This is because the (excited)



Fig. 7. Energy diagram for explanation of the Franck-Condon principle. The potential wells show favored transitions between vibrational sublevels v = 0 and v = 2 both for absorption (blue arrow) and emission (green arrow) [5].

singlet-triplet and triplet-singlet (ground state) transitions involve spin-forbidden transitions. Longlasting phosphorescence (milliseconds to seconds) from this state can be seen in stiff solution or in deoxygenated solutions. The French physicist Edmond Becquerel, who created a device he dubbed a phosphoroscope in 1857, is likely the source of the term "phosphorescence".

He may use this device to gauge how long it takes for a phosphorescent sample to quit glowing after being excited. The triplet state of an aromatic molecule is the starting point for photochemical reactions due to its prolonged lifespan. The generation of highly reactive singlet oxygen is one reaction in particular that is notable. The ground state of the oxygen molecule, O2, is a triplet. When an aromatic molecule in the triplet state repeatedly collides with oxygen in solution, energy is transferred and singlet oxygen is produced, which has the ability to oxidize (and ultimately kill) the aromatic molecule [5].

# 1.5. Vibrational energy levels of polyatomic molecules

Polyatomic molecules oscillate at frequencies that are complicated, whether they are linear or nonlinear. Due to the incompatibility of molecular vibrations, the infrared spectrum encompasses fundamental oscillation frequencies, suprabasic frequencies, and (mixed bands) [6]. Because of this, descriptive approaches for analyzing the problem of molecular oscillations have been created. These methods involve counting the number of regular shapes for each type of symmetry originating from the vibrational motion of the molecule and for each group of corresponding internal coordinates.

As well as how the constants are related to the masses of the atoms, the lengths of the bonds, and the frequencies of these oscillations that may be acquired by experiment. Scientist E.B. Wilson was able to explain the vibrational motion using the strength of mono bonds, angles between bonds, and the matrices F and G, where (F) is the matrix of force constants that completely captures the geometrical distribution of the particle. Additionally, (G) matrix with clusters, special spare relationships for seeds, and Wilson ability to be provided by relationship [7,8].

$$\Sigma L_{j} (F_{ij} - \lambda G_{ij}) \tag{1}$$

Where  $F_{ij}$  stands for the force constants matrix element, which introduces oscillation's potential energy into the equation even, though

$$F_{ij} \sum_{j}^{3N} \sum_{i}^{3N} \frac{1}{2} V = R_i R_j$$
(2)

G<sub>ij</sub>: is an element of the atomic mass matrix that brings kinetic energy into the equation since:

$$\Gamma = \frac{1}{2} \sum_{i}^{3N} \sum_{j}^{3N} G_{ij} R_{i}^{\circ} R_{j}^{\circ}$$
(3)

The eigenvalue function brings the frequency to the equation and is given by  $\lambda$ 

$$\lambda = 4\pi^2 c^2 v^2 \tag{4}$$

Where.

c: is the speed of light.

v: Harmonic vibration frequency in  $cm^{-1}$ .

 $L_i$ : The values of the Eigenvectors Coefficients describing the oscillating coordinate. Note that  $R_i$  and  $R_j$  represent any internal coordinate (such as the length of an axis, an angle, an angle of planes, a Cartesian (x,y,z) coordinate, or any other coordinate [9].

Zhe Chen and his groupe in (2007) found that total internal reflection synchronous Fluoresceence spectroscopy (TIRSF) is applied successfully to investigate Rhodamine 6G (R6G) at the silica/water interface [10]. (I.T. Sugiarto, Isnaeni and K Y Putri, 2017), is using the R6G as a tracer dye in water to determine the rate and direction of flow and transport [11]. (S. A. Tomása, S. Stolik and others..., 2005), they are study optical properties of the films were characterized by photoacoustic, excitation, and fluorescence spectroscopies, when \_TiO2\_ thin films doped with Rhodamine 6G \_R6G\_ were deposited on glass substrates by the sol-gel process [12]. (Alkadhimi, Abbas and others ...., 2020) They studied the physical properties of Rhodamine 6Gpolyvinylalcohol (Rh6G/PVA) films were prepared by casting method at room temperature, the energy bandgap is slightly affected by the addition of a R6G dye solution. R6G/PVA films showed due to red shift and energy bandgap reduction. The results showed that the best sensitivity calculated at 40 °C for the grown Rh6G (15 ml)/PVA film is about 35.74 % [13].

Through the above, we note the great importance that dyes play in modern laser applications and keep pace with the rapid development of modern technology that has conquered the world with its applications in medicine, engineering, robotics, whether giant or micro, industry, agriculture and. Which led to interest Using it and increasing the research of scientists and researchers in their studies to learn more about the properties of Rhodamine 6G and the properties of dyes.

# 2. Results and calculations

Software used in the search
 A-CS CHEM Office Pro 2000 for accounts.

 B-CS Chem Draw 5.0 Manu for drawing
 2- The studied research molecule

## **Constitution:**

2-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl] benzoic acidthe monohydrochloride of -ethyl ester

C28H31N2O3Cl · MW: 479.02. Characteristics:

Red, crystalline solid appearance Maximum absorption (in ethanol): 530 nm  $10.50 \times 104 \text{ L mol}^{-1} \text{ cm}^{-1}$  is the molar absorptivity. Maximum fluorescence in ethanol: 556 nm [14].

From Fig. (8), representing the molecular structure of Rhodamine 6G.

### 3. Bond length calculate

The effects of effective components are calculated in the molecule using a program CS CHEM Office Pro 2000. As in Table (2), we note that the length of the  $[C_{(1)}-C_{(6)}](1.561 \text{ A})$  bonds, which is a double bond, is shorter than the successive  $[C_{(1)}-C_{(2)}](1.620 \text{ A})$  bond, and the  $[C_{(1)}-N_{(32)}](1.601 \text{ A})$  bond, they are two singles, and the  $[C_{(2)}-C_{(3)}](1.453 \text{ A})$  bond, which is a double bond, and shorter than the  $[C_{(1)}-N_{(32)}](1.601 \text{ A})$  and  $[C_{(2)}-C_{(4)}](1.737 \text{ A})$ , they are two singles, and so on with the rest of the other double bonds such as  $[C_{(4)}-C_{(5)}]$ ,  $[C_{(7)}-C_{(8)}]$ ,  $[C_{(9)}-C_{(14)}]$ ,  $[C_{(11)}-C_{(12)}]$ ,  $[C_{(13)}-N_{(22)}]$ ,  $[C_{(15)}-C_{(18)}]$ ,  $[C_{(16)}-C_{(21)}]$ ,  $[C_{(18)}-H_{(63)}]$ .

# 4. Heat of formation

Heat of Formation of the bonds of the Rhodamine 6G dye was calculated as in Table (3). Heat of Formation values of the double bonds was the highest value of the Heat of Formation values of the single bonds, as:  $[C_{(1)}-C_{(6)}](-164.54321 \text{ kcal/mol})$ ,  $[C_{(2)}-C_{(3)}](-164.987045 \text{ kcal/mol})$ ,  $[C_{(4)}-C_{(5)}](-164.676432 \text{ kcal/mol})$ ,  $[C_{(7)}-C_{(8)}](-165.657865 \text{ kcal/mol})$ ,  $[C_{(9)}-C_{(14)}](-164.099865 \text{ kcal/mol})$ ,  $[C_{(11)}-C_{(12)}](-164.900091 \text{ kcal/mol})$ ,  $[C_{(13)}-N_{(22)}](-164.654309 \text{ kcal/mol})$ ,  $[C_{(15)}-C_{(18)}](165.09432 \text{ kcal/mol})$ ,  $[C_{(16)}-C_{(21)}]$  (164.654320 kcal/mol),  $[C_{(18)}-H_{(63)}](-166.48321 \text{ kcal/mol})$ .

# 5. Calculating the constants of forces

The Force Constants were calculated as in Table (4) using the a program CS CHEM Office Pro 2000, and it was found that the double bond constant  $[C_{(1)}-C_{(6)}](9.43276 \text{ m. dyne/A})$  is higher and greater than the constant of the forces for the rest of the other bonds, such as the single bond



Fig. 8. Representing the molecular structure of Rhodamine 6G [14].

BOND	LENGTH OF BOND (A )	TYPE OF BOND	BOND	LENGTH OF BOND (A°)	TYPE OF BOND	BOND	LENGTH OF BOND (A°)	TYPE OF BOND
C(1)-C(2)	1.620	SINGLE	C(12)-C(45)	1.674	SINGLE	C(28)-H(29)	1.723	SINGLE
C(1)-C(6)	1.561	DOUBLE	C(13)-C(14)	1.645	SINGLE	C(28)-H(30)	1.652	SINGLE
$C_{(1)} - N_{(32)}$	1.601	SINGLE	$C_{(13)} - N_{(22)}$	1.457	DOUBLE	$N_{(32)} - C_{(38)}$	1.743	SINGLE
$C_{(2)} - C_{(3)}$	1.453	DOUBLE	$C_{(14)} - H_{(61)}$	1.700	SINGLE	$N_{(32)} - H_{(33)}$	1.667	SINGLE
$C_{(2)} - C_{(4)}$	1.737	SINGLE	C(15)-C(16)	1.699	SINGLE	C(34)-C(38)	1.643	SINGLE
$C_{(3)} - C_{(4)}$	1.721	SINGLE	$C_{(15)} - C_{(18)}$	1.468	DOUBLE	$C_{(34)} - H_{(35)}$	1.743	SINGLE
C(3)-H(65)	1.679	SINGLE	$C_{(16)} - C_{(21)}$	1.455	DOUBLE	C(34)-H(38)	1.689	SINGLE
$C_{(4)} - C_{(5)}$	1.474	DOUBLE	$C_{(11)} - C_{(52)}$	1.711	SINGLE	$C_{(34)} - H_{(37)}$	1.743	SINGLE
$C_{(4)} - C_{(7)}$	1.699	SINGLE	C(18)-C(19)	1.656	SINGLE	C(38)-H(39)	1.751	SINGLE
$C_{(5)} - C_{(6)}$	1.625	SINGLE	C(18)-H(63)	1.437	DOUBLE	C(38)-H(40)	1.753	SINGLE
$C_{(5)} - O_{(10)}$	1.631	SINGLE	$C_{(19)} - C_{(20)}$	1.699	SINGLE	$C_{(41)} - H_{(42)}$	1.731	SINGLE
C <sub>(6)</sub> -H <sub>(64)</sub>	1.624	SINGLE	C(19)-H(62)	1.712	SINGLE	C(41)-H(43)	1.765	SINGLE
$C_{(7)} - C_{(8)}$	1.438	DOUBLE	$C_{(20)} - C_{(21)}$	1.730	SINGLE	$C_{(41)} - H_{(44)}$	1.722	SINGLE
$C_{(7)} - C_{(15)}$	1.635	SINGLE	C(20)-H(59)	1.721	SINGLE	C(45)-H(46)	1.699	SINGLE
$C_{(8)} - C_{(9)}$	1.674	SINGLE	$C_{(21)} - H_{(60)}$	1.698	SINGLE	$C_{(45)} - H_{(47)}$	1.661	SINGLE
$C_{(8)} - C_{(11)}$	1.681	SINGLE	$N_{(22)} - C_{(28)}$	1.754	SINGLE	$C_{(45)} - H_{(48)}$	1.772	SINGLE
C <sub>(9)</sub> -O <sub>(10)</sub>	1.654	SINGLE	$N_{(22)} - H_{(23)}$	1.732	SINGLE	$C_{(52)} - H_{(53)}$	1.649	SINGLE
$C_{(9)} - C_{(14)}$	1.123	DOUBLE	$C_{(24)} - C_{(28)}$	1.677	SINGLE	$C_{(52)} - H_{(54)}$	1.741	SINGLE
$C_{(11)} - C_{(12)}$	1.466	DOUBLE	$C_{(24)} - H_{(25)}$	1.700	SINGLE	$C_{(52)} - H_{(55)}$	1.744	SINGLE
$C_{(11)} - H_{(17)}$	1.701	SINGLE	$C_{(24)} - H_{(26)}$	1.674	SINGLE	O(49)-H(57)	1.699	SINGLE
$C_{(12)} - C_{(13)}$	1.675	SINGLE	C <sub>(24)</sub> -H <sub>(27)</sub>	1.645	SINGLE	O <sub>(49)</sub> -H <sub>(58)</sub>	1.768	SINGLE

Table 2. Shows the bond lengths between C, N, H, O atoms of Rhodamine 6 G.

Table 3. The Heat of formation values the Bonds of Rhodamine 6 G.

BOND	H.O.F.	BOND	H.O.F.	BOND	H.O.F.
	Kcal/mol		Kcal/mol		Kcal/mol
$C_{(1)} - C_{(2)}$	-171.09987	$C_{(12)} - C_{(45)}$	-170.76595	C(28)-H(29)	-168.65488
C(1)-C(6)	-164.54321	$C_{(13)} - C_{(14)}$	-169.88887	C(28)-H(30)	-169.45620
C(1)-N(32)	-170.02317	$C_{(13)} - N_{(22)}$	-164.65430	$N_{(32)} - C_{(38)}$	-171.44321
$C_{(2)} - C_{(3)}$	-164.98704	$C_{(14)} - H_{(61)}$	-168.87654	$N_{(32)} - H_{(33)}$	-169.99087
C(2)-C(4)	-169.43765	$C_{(15)} - C_{(16)}$	-170.12134	$C_{(34)} - C_{(38)}$	-170.55667
C <sub>(3)</sub> -C <sub>(4)</sub>	-169.89743	$C_{(15)} - C_{(18)}$	-165.09432	C <sub>(34)</sub> -H <sub>(35)</sub>	-169.56432
C(3)-H(65)	-169.00765	$C_{(16)} - C_{(21)}$	-164.65432	$C_{(34)} - H_{(38)}$	-168.22345
$C_{(4)} - C_{(5)}$	-164.67643	$C_{(11)} - C_{(52)}$	-171.56743	$C_{(34)} - H_{(37)}$	-171.88976
$C_{(4)} - C_{(7)}$	-170.76543	$C_{(18)} - C_{(19)}$	-168.56432	C(38)-H(39)	-170.55678
$C_{(5)} - C_{(6)}$	-168.99876	C(18)-H(63)	-166.48321	C(38)-H(40)	-168.66543
C(5)-O(10)	-169.77654	$C_{(19)} - C_{(20)}$	-165.97609	$C_{(41)} - H_{(42)}$	-169.90092
C(6)-H(64)	-170.65432	$C_{(19)} - H_{(62)}$	-171.89023	$C_{(41)} - H_{(43)}$	-171.34345
$C_{(7)} - C_{(8)}$	-165.56786	$C_{(20)} - C_{(21)}$	-168.77786	$C_{(41)} - H_{(44)}$	-168.37890
$C_{(7)} - C_{(15)}$	-171.89900	C(20)-H(59)	-171.32177	C(45)-H(46)	-169.54329
C <sub>(8)</sub> -C <sub>(9)</sub>	-169.99871	$C_{(21)} - H_{(60)}$	-170.77765	$C_{(45)} - H_{(47)}$	-168.54630
$C_{(8)} - C_{(11)}$	-169.33781	$N_{(22)} - C_{(28)}$	-170.90091	$C_{(45)} - H_{(48)}$	-171.89765
C <sub>(9)</sub> -O <sub>(10)</sub>	-170.99543	N(22)-H(23)	-169.77654	C(52)-H(53)	-168.09908
$C_{(9)} - C_{(14)}$	-164.09986	$C_{(24)} - C_{(28)}$	-168.66554	$C_{(52)} - H_{(54)}$	-171.22314
C(11)-C(12)	-164.90009	$C_{(24)} - H_{(25)}$	-171.87696	$C_{(52)} - H_{(55)}$	-168.33426
C(11)-H(17)	-168.01542	$C_{(24)} - H_{(26)}$	-170.23156	O <sub>(49)</sub> -H <sub>(57)</sub>	-171.54090
C(12)-C(13)	-171.88564	C(24)-H(27)	-171.09876	O(49)-H(58)	-170.33456

 $[C_{(1)}-C_{(2)}](3.87652 \text{ m. dyne/A})$ , and greater than the double bond constant, and so with the rest of the bonds  $[C_{(2)}-C_{(3)}](8.07654 \text{ m. dyne/A})$ , and we also note that the constants of forces Double bonds are greater than the constants of forces for single bonds because the bonding type in double bonds is  $sp^2$ , which is stronger than the bonding type in single bonds, which is  $sp^3$ .

# 6. Vibrational patterns of rhodamine 6G bonds

The vibrational patterns shown in Table (5) were calculated and were as follows:

a- 1-Vibrational patterns of the Double bond [C=C]:

BOND	Constant Force m.dyne/A	BOND	Constant Force m.dyne/A°	BOND	Constant Force m.dyne/A°
C <sub>(1)</sub> -C <sub>(2)</sub>	3.87652	C <sub>(12)</sub> -C <sub>(45)</sub>	5.9987	C(28)-H(29)	5.8999
C(1)-C(6)	9.43276	$C_{(13)} - C_{(14)}$	4.9998	C(28)-H(30)	4.9689
$C_{(1)} - N_{(32)}$	5.87652	$C_{(13)} - N_{(22)}$	8.0832	N(32)-C(38)	4.6544
$C_{(2)} - C_{(3)}$	8.07654	$C_{(14)} - H_{(61)}$	5.8765	$N_{(32)} - H_{(33)}$	5.8765
$C_{(2)} - C_{(4)}$	3.76543	$C_{(15)} - C_{(16)}$	5.8832	$C_{(34)} - C_{(38)}$	5.1121
$C_{(3)} - C_{(4)}$	6.98701	$C_{(15)} - C_{(18)}$	8.0876	$C_{(34)} - H_{(35)}$	5.0955
C(3)-H(65)	5.87622	$C_{(16)} - C_{(21)}$	8.8889	C(34)-H(38)	5.0015
$C_{(4)} - C_{(5)}$	8.95361	$C_{(11)} - C_{(52)}$	5.8765	$C_{(34)} - H_{(37)}$	5.3216
C <sub>(4)</sub> -C <sub>(7)</sub>	5.67770	C(18)-C(19)	5.6755	C(38)-H(39)	4.9999
$C_{(5)} - C_{(6)}$	5.8942	$C_{(18)} - H_{(63)}$	4.7631	$C_{(38)} - H_{(40)}$	5.0001
$C_{(5)} - O_{(10)}$	6.9002	$C_{(19)} - C_{(20)}$	8.0334	$C_{(41)} - H_{(42)}$	5.75432
$C_{(6)} - H_{(64)}$	4.3456	$C_{(19)} - H_{(62)}$	5.8762	$C_{(41)} - H_{(43)}$	4.8876
$C_{(7)} - C_{(8)}$	8.0321	$C_{(20)} - C_{(21)}$	5.9872	$C_{(41)} - H_{(44)}$	4.9087
$C_{(7)} - C_{(15)}$	5.8943	C(20)-H(59)	4.8822	C(45)-H(46)	4.9990
$C_{(8)} - C_{(9)}$	4.8943	$C_{(21)} - H_{(60)}$	5.9876	$C_{(45)} - H_{(47)}$	5.5432
$C_{(8)} - C_{(11)}$	5.3219	$N_{(22)} - C_{(28)}$	6.1107	$C_{(45)} - H_{(48)}$	5.9090
$C_{(9)} - O_{(10)}$	5.5562	$N_{(22)} - H_{(23)}$	5.7643	$C_{(52)} - H_{(53)}$	4.9992
$C_{(9)} - C_{(14)}$	7.9999	$C_{(24)} - C_{(28)}$	6.0001	$C_{(52)} - H_{(54)}$	4.9765
$C_{(11)} - C_{(12)}$	8.0965	$C_{(24)} - H_{(25)}$	6.0011	C(52)-H(55)	5.7654
C(11)-H(17)	4.7654	$C_{(24)} - H_{(26)}$	5.8880	O(49)-H(57)	4.9898
C <sub>(12)</sub> -C <sub>(13)</sub>	5.3876	C(24)-H(27)	5.8765	O(49)-H(58)	5.0012

Table 4. Shows the Constant of Forces for the bonds of Rhodamine 6G dye.

The double bond [C=C] has nine. Stretch vibratory patterns  $[C=C]_{str}$  sandwiched between the-range (2.1756–2.2419) cm<sup>-1</sup>, nine-bending-vibratory-patterns-mode  $[C=C]_{ben}$ .sandwiched-between-the-range-(16.5396–16.6623) cm<sup>-1</sup>, and-nine-Stretch-bending-vibratory-modes  $[C=C]_{str-ben}$ . Sandwiched between the (0.1652–0.1738) cm<sup>-1</sup>.

#### 2- Vibrational patterns of the Single bond [C–C]:

The single bond [C-C] has eighteen stretch vibratory patterns  $[C-C]_{str}$  sandwiched between the range (2.1730–2.2222) cm<sup>-1</sup>, eighteen bending vibratory patterns modes  $[C-C]_{ben}$ . Sandwiched between the range (16.6562-16.5390) cm<sup>-1</sup>, and eighteen stretch-bending vibratory modes  $[C-C]_{str.-ben}$ . Sandwiched between the (0.1599–0.1738) cm<sup>-1</sup>.

# b- 1-Vibrational patterns of the double bond [C= N]:

The double bond  $[C_{(13)} = N_{(22)}]$  has single stretching vibrational Mode (2.1761) cm<sup>-1</sup>, single bending vibratory pattern (16.5416) cm<sup>-1</sup>, and single Stretch-bending vibratory modes (0.1704) cm<sup>-1</sup>.

#### 2- Vibrational patterns of the single bond [C–N]:

A single bond  $[C_{(1)}-N_{(32)}]$  has single stretching vibrational mode (2.2062) cm<sup>-1</sup>, single bending vibratory pattern (16.6442) cm<sup>-1</sup>, and single stretchbending vibratory modes (0.1682) cm<sup>-1</sup>.

#### c- Vibratory modes of the single [N–C]:

Has two stretching vibrational modes of magnitude (2.1756) cm<sup>-1</sup>, and two bending vibrational modes of magnitude (16.5391,16.5392) cm<sup>-1</sup> and two stretch - bending vibrational modes of magnitude (0.1702,0.1699) cm<sup>-1</sup>.

### d- 1-Vibratory modes of the double [C=H]:

A double bond  $[C_{(18)}-H_{(63)}]$  has single stretching vibrational mode (2.1762) cm<sup>-1</sup>, single bending vibratory pattern (16.5398) cm<sup>-1</sup>, and single stretchbending vibratory modes (0.1705) cm<sup>-1</sup>

#### 2- Vibratory modes of the single [C-H]:

Twenty-six have an stretching vibrational pattern sandwiched between the range (2.1752–2.2970) cm<sup>-1</sup>, twenty-six have an bending vibrational pattern sandwiched between the range (16.5390–16.6407) cm<sup>-1</sup> and twenty-six have an stretching -bending vibrational pattern sandwiched between the range (0.1690–0.1719) cm<sup>-1</sup>

### e- Vibratory modes of the single [N-H]:

Has two stretching vibrational modes of magnitude (2.1759,2.1761) cm<sup>-1</sup>, and two bending vibrational modes of magnitude (16.5398,16.5401) cm<sup>-1</sup> and two stretch-bending vibrational modes of magnitude (0.1700,0.1703) cm<sup>-1</sup>.

BOND	التردد	التردد الاهتزازي	التردد	BOND	التردد	التردد	التردد
	الاهتزازي الامتطائي	الاانحنائ	ال اهتز از ي		الاهتزازي الامتطائي	الاهتزازي	الااهتزازي
	Stretech	Bending	الاامتطائي- الاانحنائي		Stretech	الاانحنائي	الامتطائي- الانحنائي
	cm <sup>-1</sup>	cm <sup>-1</sup>	Stretech –Bending		cm <sup>-1</sup>	Bending	Stretech -Bending
			cm <sup>-1</sup>			cm <sup>-1</sup>	cm <sup>-1</sup>
C <sub>(1)</sub> -C <sub>(2)</sub>	2.2202	16.6562	0.1638	C(19)-H(62)	2.1761	16.5491	0.1699
$C_{(1)} - C_{(6)}$	2.2149	16.6476	0.1652	$C_{(20)} - C_{(21)}$	2.1760	16.5403	0.1704
$C_{(1)} - N_{(32)}$	2.2062	16.6442	0.1682	C(20)-H(59)	2.1758	16.5390	0.1699
C(2)-C(3)	2.2419	16.6623	0.1687	C(21)-H(60)	2.1757	16.5404	0.1703
$C_{(2)} - C_{(4)}$	2.1880	16.6437	0.1721	$N_{(22)} - C_{(28)}$	2.1756	16.5391	0.1699
$C_{(3)} - C_{(4)}$	2.1885	16.6389	0.1728	N(22)-H(23)	2.1759	16.5401	0.1703
C(3)-H(65)	2.1970	16.6407	0.1690	$C_{(24)} - C_{(28)}$	2.1757	16.5390	0.1698
$C_{(4)} - C_{(5)}$	2.2236	16.6285	0.1689	$C_{(24)} - H_{(25)}$	2.1757	16.5404	0.1702
$C_{(4)} - C_{(7)}$	2.2222	16.6474	0.1599	C(24)-H(26)	2.1756	16.5390	0.1699
$C_{(5)} - C_{(6)}$	2.2119	16.6385	0.1634	$C_{(24)} - H_{(27)}$	2.1761	16.5399	0.1702
C(5)-O(10)	2.2048	16.6238	0.1670	C(28)-H(29)	2.1756	16.5390	0.1698
C <sub>(6)</sub> -H <sub>(64)</sub>	2.1949	16.5701	0.1719	$C_{(28)} - H_{(30)}$	2.1762	16.5398	0.1702
$C_{(7)} - C_{(8)}$	2.1854	16.5549	0.1738	N(32)-C(38)	2.1756	16.5392	0.1702
$C_{(7)} - C_{(15)}$	2.1824	16.5434	0.1738	N(32)-H(33)	2.1761	16.5398	0.1700
$C_{(8)} - C_{(9)}$	2.1738	16.5652	0.1709	$C_{(34)} - C_{(38)}$	2.1765	16.5390	0.1701
C <sub>(8)</sub> -C <sub>(11)</sub>	2.1730	16.5513	0.1700	C(34)-H(35)	2.1759	16.5398	0.1699
C <sub>(9)</sub> -O <sub>(10)</sub>	2.1781	16.5384	0.1708	$C_{(34)} - H_{(38)}$	2.1753	16.5392	0.1701
$C_{(9)} - C_{(14)}$	2.1756	16.5439	0.1709	C(34)-H(37)	2.1758	16.5396	0.1699
$C_{(11)} - C_{(12)}$	2.1767	16.5405	0.1700	$C_{(38)} - H_{(39)}$	2.1754	16.5391	0.1699
C(11)-H(17)	2.1760	16.5423	0.1708	C(38)-H(40)	2.1755	16.5399	0.1700
$C_{(12)} - C_{(13)}$	2.1765	16.5403	0.1700	$C_{(41)} - H_{(42)}$	2.1754	16.5392	0.1699
$C_{(12)} - C_{(45)}$	2.1762	16.5418	0.1708	$C_{(41)} - H_{(43)}$	2.1756	16.5400	0.1698
C(13)-C(14)	2.1764	16.5400	0.1700	C(41)-H(44)	2.1752	16.5391	0.1700
$C_{(13)} - N_{(22)}$	2.1761	16.5416	0.1704	$C_{(45)}$ - $H_{(46)}$	2.1752	16.5401	0.1699
C(14)-H(61)	2.1762	16.5400	0.1701	C(45)-H(47)	2.1752	16.5390	0.1701
C(15)-C(16)	2.1761	16.5414	0.1705	$C_{(45)} - H_{(48)}$	2.1752	16.5402	0.1699
$C_{(15)} - C_{(18)}$	2.1762	16.5396	0.1700	$C_{(52)} - H_{(53)}$	2.1753	16.5402	0.1701
C(16)-C(21)	2.1762	16.5413	0.1705	C(52)-H(54)	2.1754	16.5387	0.1699
$C_{(11)} - C_{(52)}$	2.1763	16.5396	0.1700	$C_{(52)} - H_{(55)}$	2.1754	16.5398	0.1701
C(18)-C(19)	2.1761	16.5411	0.1705	O(49)-H(57)	2.1755	16.5389	0.1699
C(18)-H(63)	2.1762	16.5397	0.1700	O(49)-H(58)	2.1756	16.5398	0.1701
C(19)-C(20)	2.1762	16.5398	0.1705				

Table 5. Represent the stretche vibrational modes, bending vibrational modes and stretche-bending vibrational modes of Rhodammine 6G.

# f- Vibratory modes of the single [O-H]:

Has two stretching vibrational modes of magnitude (2.1756,2.1755) cm<sup>-1</sup>, and two bending vibrational modes of magnitude (16.5389, 16.5398) cm<sup>-1</sup> and two stretch - bending vibrational modes of magnitude (0.1699,0.1701) cm<sup>-1</sup>.

g- Vibratory modes of has two stretching vibrational modes of magnitude (2.1781,2.2048) cm<sup>-1</sup>, and two bending vibrational modes of magnitude (16.5384–16.6238) cm<sup>-1</sup> and two stretch - bending vibrational modes of magnitude (0.1708-0.1670)  $\text{cm}^{-1}$ .

The single [C-O]:

# 7. Calculation of the energy levels of HOMO–LUMO

The energy of the HOMO–LUMO levels was calculated, as the dye contains (87)energy levels of HOMO and (76) energy levels of LUMO, as shown in Table (6), which shows the number of electrons,

Table 6. Shows the energy levels in HOMO-LUMO for Rhodammine 6G.

NO. Lev	el	NO. Electron		Energy (eV)		NO. Level		NO. Electron		Energy (eV)	
LUMO	HOMO	LUMO	HOMO	LUMO	НОМО	LUMO	НОМО	LUMO	HOMO	LUMO	НОМО
1	-1	90	87	-0.322894	-4.771973	46	-46	135	42	77.148185	-23.472349
2	-2	91	86	0.204845	-5.962919	47	-47	136	41	80.469474	-23.767637
3	-3	92	85	0.415127	-7.131094	48	-48	137	40	82.376370	-23.893177
4	-4	93	84	1.678155	-7.981585	49	-49	138	39	84.947803	-24.079755
5	-5	94	83	3.067828	-8.646156	50	-50	139	38	89.560357	-24.227148
6	-6	95	82	6.529933	-9.554852	51	-51	140	37	98.498489	-24.754026
7	-7	96	81	9.844781	-10.39359	52	-52	141	36	99.375278	-25.300455
8	-8	97	80	10.321422	-10.604058	53	-53	142	35	106.056136	-25.354589
9	-9	98	79	12.535167	-11.301064	54	-54	143	34	106.872468	-25.537640
10	-10	99	78	14.000293	-11.424118	55	-55	144	33	115.263957	-26.138341
11	-11	100	77	19.570758	-11.978076	56	-56	145	32	118.912110	-26.361641
12	-12	101	76	26.783868	-12.390211	57	-57	146	31	126.605330	-27.248669
13	-13	102	75	30.877207	-12.632628	58	-58	147	30	133.302547	-27.587400
14	-14	103	74	32.061942	-13.014961	59	-59	148	29	135.834713	-28.161757
15	-15	104	73	33.244524	-14.124939	60	-60	149	28	134.921136	-28.438382
16	-16	105	72	35.982835	-14.451622	61	-61	150	27	150.239940	-28.703702
17	-17	106	71	36.367842	-14.848050	62	-62	151	26	153.669776	-30.056327
18	-18	107	70	37.957724	-14.940863	63	-63	152	25	164.134866	-30.459482
19	-19	108	69	38.857652	-15.474210	64	-64	153	24	169.871691	-30.819520
20	-20	109	68	39.582652	-15.725340	65	-65	154	23	180.911453	-32.118890
21	-21	110	67	39.927591	-16.041526	66	-66	155	22	182.332943	-32.294997
22	-22	111	66	40.660012	-16.818989	67	-67	156	21	200.180488	-32.615176
23	-23	112	65	42.467232	-16.996872	68	-68	157	20	201.973105	-33.482196
24	-24	113	64	42.842692	-17.127729	69	-69	158	19	213.941860	-34.192290
25	-25	114	63	43.876868	-17.505484	70	-70	159	18	226.849189	-35.570683
26	-26	115	62	43.931018	-17.953849	71	-71	160	17	238.464963	-36.277244
27	-27	116	61	44.592479	-18.269796	72	-72	161	16	249.250812	-37.690605
28	-28	117	60	47.499147	-18.430996	73	-73	162	15	261.896573	-38.532299
29	-29	118	59	47.985857	-18.637959	74	-74	163	14	283.811106	-38.966810
30	-30	119	58	48.447102	-18.745687	75	-75	164	13	888.981772	-39.947446
31	-31	120	57	51.395784	-19.186950	76	-76	165	12	1763.67056	-40.531429
32	-32	121	56	52.990381	-19.525810	-	-77	-	11	_	-41.066575
33	-33	122	55	53.174538	-19.770092	-	-78	-	10	_	-42.517809
34	-34	123	54	53.760103	-19.770094	-	-79	-	9	_	-43.619851
35	-35	124	53	56.405436	-20.132593	-	-80	-	8	_	-45.404739
36	-36	125	52	58.395593	-20.611365	-	-81	-	7	_	-46.897614
37	-37	126	51	59.607735	-20.911915	-	-82	-	6	_	-47.957504
38	-38	127	50	61.753448	-21.087888	-	-83	-	5	_	-49.764369
39	-39	128	49	64.243724	-21.327414	-	-84	-	4	_	-50.277003
40	-40	129	48	65.742415	-21.439827	-	-85	-	3	_	-53.224375
41	-41	130	47	66.203217	-21.644773	-	-86	-	2	_	-55.224375
42	-42	131	46	68.273195	-21.755579	_	-87	-	1	_	-63.723685
43	-43	132	45	69.822511	-22.321860						
44	-44	133	44	71.873705	-22.362877						
45	-45	134	43	74.462301	-23.168098						



Fig. 9. HOMO-LUMO shapes, which shows the high efficiency and effect of carbon atoms significantly on the Rhodammine 6G dye.

in addition to the illustration using the (CS Chem Draw 5.0) program in Fig. (9), which shows the high efficiency and influence of carbon atoms in a way big on dye.

# 7.1. Conclusion

- 1- CS CHEM Office Pro 2000 program can be adopted to obtain good results for the study of some large molecules with high energy content, which are difficult to use in the laboratory due to their sensitivity, danger and speed of reaction.
- 2- Possession of the dye sixty-three bonds, ten double and fifty-three single, most double bonds are shorter in length than single ones, and this feature made the dye strength and durability. Double bonds have greater heat of formation and force constants than Single bonds.

- 3- The possession of the bonds in Rhodamine 6G dye of the vibrational patterns and the stretching frequencies and the stretching-bending frequencies together indicate the intensity of the activity and effectiveness of these bonds.
- 4- To compare some physical properties of double and single bonds through the following table

The Bond	Length of Bond (A°)	H.O.F. Kcal/mol	Constant Force (m.dyne/A°)	Electronic Cloud Gathering
Single	Longer	Less	The least	Least assembled
Double	Shorter	Higher	Greatest	Most gathered

5- During the HOMO–LUMO calculations, we notice that the electronic cloud gathers around the Double Carbon [C=C]bond, It is a great evidence of the effect of carbon on the Rhoda-mine 6G dye.

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