Journal of Kufa for Chemical Sciences
ISSN(P) :2077-2351 ISSN(E): 3006-3280
Journal Homepage:
https://journal.uokufa.edu.iq/index.php/jkcs/index

Article

Study Optical Properties of New β-Aminocarbonyl Compound

Hanan F. Al-Shamsi[1)], Khansa Abdul Razzaq AliAl-Assadi[2)] Hanoy K. Al-Amood[3a)]

[1]Department of Pharmaceutical Chemistry, College of Pharmacy, University of Basrah

[2,3] Department of Chemistry, College of Sciences, University of Basrah

Corresponding [an] E-mail: hanoy.alamood@uobasrah.edu.iqod@uobasrah.edu.iq

Abstract: One new compound from the beta - aminocarbonyl group named 3-((4-bromophenyl)amino)-3-(2,4-dichlorophenyl)-1-(3-methoxyphenyl)propan-1-one has been synthesized. FT-IR, Mass, 13C, and 1H-NMR spectroscopy techniques identified the synthesis compound. The physical properties of the 3p-Br compound were studied, and it was proven to behave as a semiconductor. We doped it with two dyes, Rhodamine 6G, and Vinyl Crystal, to study the effect of increasing the doping concentration on the band gap and thus on the conductivity on conductivity. It was observed that the energy gap decreased with increasing concentration. This was proven by conducting FTIR, PL, and DRS spectroscopy.

Keywords: beta-amino carbonyl compound, chalcone, Aza-Michael addition reaction, PL, and DRS spectroscopy.

INTRODUCTION

Semiconductors are crystalline, potent substances with a covalent bond structure with electrical conductivity between a conductor and an insulator.[1]. They can behave strongly, but not as well as conductors. They are crystalline and incorporate very few unfastened electrons at room temperature. This restricted number of unbound electrons in semiconductors is because of their electricity band structure(which is the power distinction among the valence band (wherein electrons are tightly bound to the atoms and are not capable of moving freely), and the conduction bands, wherein electrons have enough energy to move freely and conduct energy). In summary, the strength hole or bandgap of semiconductors is the difference in electricity between the valence band and the conduction band in semiconductors. The electricity hole is tiny compared to insulators, however larger than conductors as in Figure 1)[2].

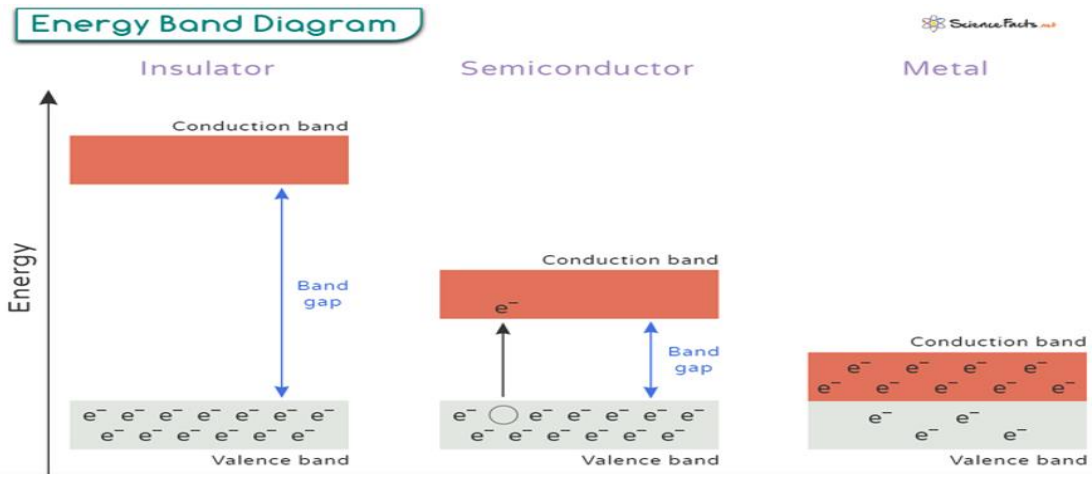


Figure (1) shows the electronic band structure of insulators, semiconductors, and metals.

Semiconductors are widely used in electronic devices because of their unique properties.[3] . They can be doped to control their conductivity, allowing for the creation of transistors, which are the building blocks of modern electronics.[4] .

Materials and Methods

Materials	Purity %
Para-bromo aniline	95
Absolute methanol	99
Triethyl amine	99
n-hexane	95
Ethylacetate	99.5

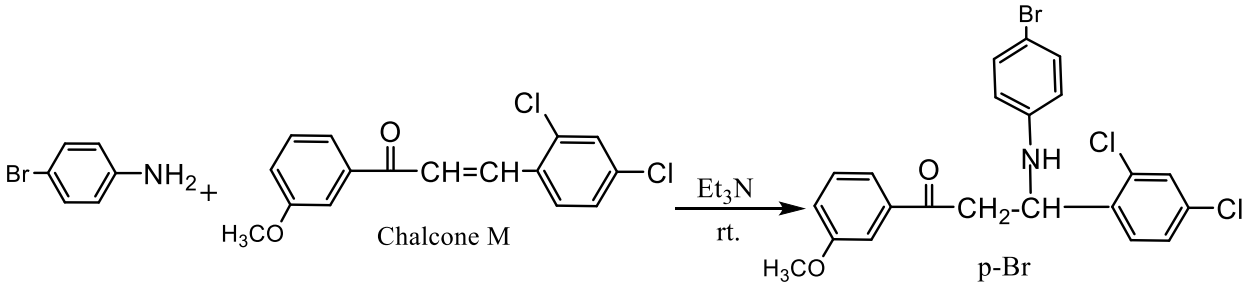
Techniques used in diagnosis

IR spectra for prepared compounds were measured as KBr disks using the Shimadzu model FT IR-8400S spectrometer at the laboratory of the Chemistry Department at Basrah University. The ^{13}C and ^{1}H- NMR spectra were recorded on a Bruker spectrometer at 300.81 MHz in DMSO-d6 as a solvent with TMS as an internal reference with mass spectra analysis at Thran University, Iran.

Preparation of compound p-Br[5]

A mixture of para-bromo aniline 1mmol (0.172gm) and chalcone (M)[6] 1 mmol (0.3 gm) was dissolved in a beaker, molality ratio (1:1), with 10 ml of absolute methanol and 1 ml of water, and in the presence of 0.4 mmol of triethyl amine as a catalyst. The reaction was carried out at room temperature with continuous stirring, Scheme (1), A gray precipitate appeared after 2 minutes. Follow up on the reaction by TLC using (n-hexane: ethylacetate (3:1)). Filter and wash with saturated sodium bicarbonate solution, and the product was recrystallized using n-hexane solvent. Mp.

134-136°C, R_f (0.4), %yield (63), IR(NH 3444, C=O 1658, Ar 3078), as figure (1), ^{1}HNMR NH (Overlap with aromatic proton 7.24-8.29), CH-NH 4.09 (S, 1H), CH_2 3.80-3.71(m, 1H), and OCH_3 3.85 (s, 3H), as figure (2), and ^{13}CNMR C=O 188.61, Ar-C-NH 159.59, C-Br 119.52, OCH3 55. 42. Mass m/z 279.1, 255, and 478, as figure (3).



Scheme (1) method of preparation of compounds

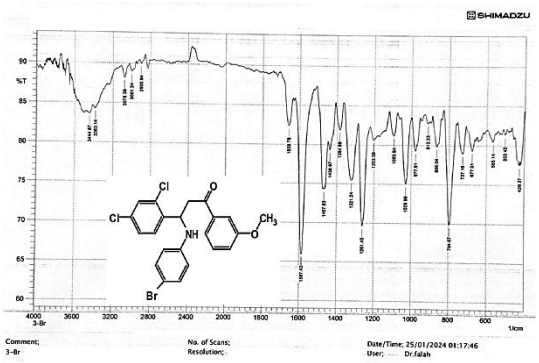


Figure (1)FT-IR Spectra of 3- pBr

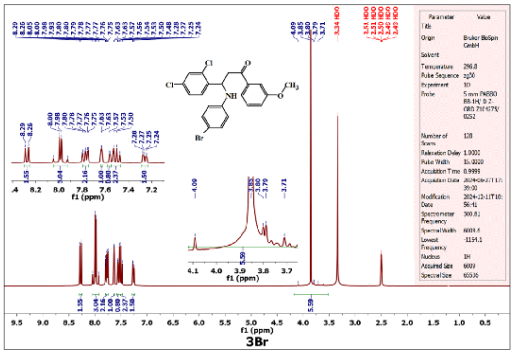


Figure (2) H^1-NMR Spectra of 3-pBr

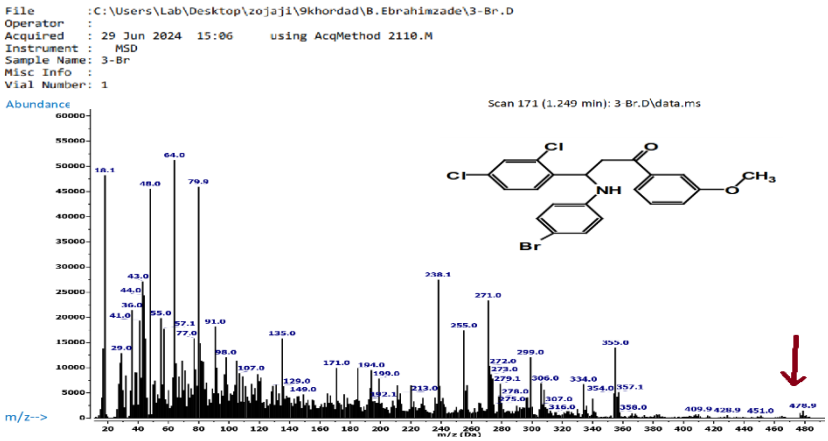


Figure (3) Mass spectrum of 3p-Br

Doping of compound 3 p-Br[7]

Doping of 3-((4-bromophenyl) amino-3-(2,4-dichlorophenyl)-1-(3-methoxyphenyl) propan-1-one with two dyes (crystal violet dyes and rhodamine G6) was made by adding the weighted dyes (0.02, 0.05, 0.07, and 0.1) to 1 gram of the compound after mixing it well (physical reaction) and dissolved in absolute methanol and DMSO, respectively, at room temperature. The mixture is poured onto a glass slide, rubbed after the precipitate dries, and used in physical measurements.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)[8, 9]

FTIR was performed for both pure 3p-Br and 3p-Br doped with different weight ratios (0.02, 0.05, 0.07, and 0.1) to 1 g with crystal violet and rhodamine 6G dyes as shown in Table (1), and figures (1), and (4a, b, c, and d). These figures show a shift in the significant specific peaks in both pure 3p-Br and doped 3p-Br, indicating physical association with the dyes. When the 3p-Br complex was adsorbed with rhodamine 6G dye and vinyl violet dye, changes occurred in the electronic environment of the complex, resulting in noticeable differences in the FT-IR spectra. The FTIR spectrum shows characteristic peaks reflecting the presence of specific functional groups, such as the carbonyl group (C=O) at about 1658 cm^{-1}, the C=C in aromatic rings at about 1587 and 1436 cm^{-1}, and the N-H band in the amine group at 3444 cm^{-1}. These peaks reflect the stable structure of the compound without the interference of external factors, while when the 3p-Br complex was adsorbed with rhodamine 6G and phenyl crystal, a slight shift in the peaks occurred; For example, the carbonyl group shifted to a higher value (1660 cm^{-1}), the aromatic rings to (1583

cm^{-1}), and (1462 cm^{-1}), and the amino group to (3430 cm^{-1}). The absorption of the dye leads to a change in the distribution of electrons around the functional groups in the organic compound, which affects the strength of the bonds and internal interactions as a result of the compound being bound to the dye by hydrogen bonds that change the intensity and position of the absorption peaks or π–π interactions that affect the aromatic regions and lead to the appearance of new peaks or modification of existing peaks[9].

Table (1) Bands of FT-IR spectra of the pure 3p-Br and 3p-Br doped with the dye

Comp.	N-H Str. (v.s)	C=O Str. (v.s)	ArC=C Str. (v.s)	C-N str (S.)	C-Br
3p-Br	3444	1658	1587 1436	1261.45	1029
V1	3430	1660	1583, 1462	1258	1031
V2	3427	1661	1581, 1463	1256	1033
V3	3425	1663	1587, 1464	1263	1035
V4	3423	1665	1588, 1465	1264	1038
R1	3430	1660	1583, 1462	1258	1031
R2	3427	1661	1585, 1463	1260	1033
R3	3425	1663	1587, 1464	1263	1035
R4	3423	1665	1588, 1465	1264	1038

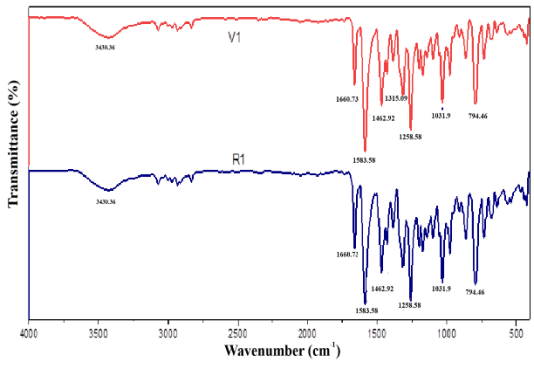


Figure (4a)FT-IR Spectra of 3p-Br doped with V1 and R1

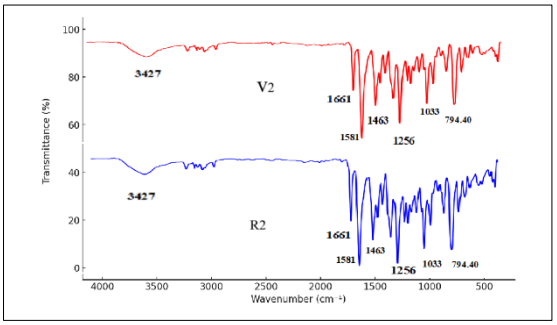


Figure (4b)FT-IR Spectra of 3p-Br doped with V2 and R2

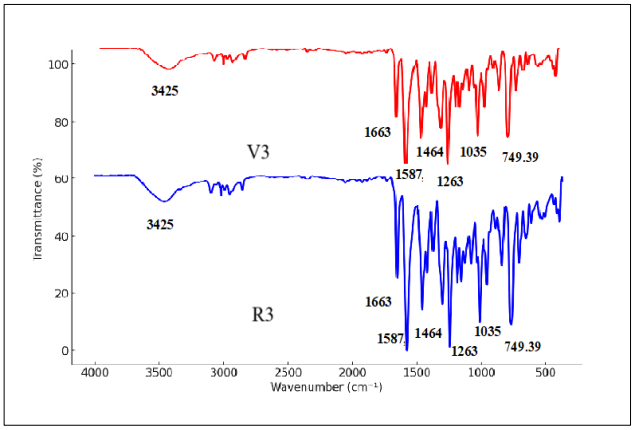


Figure (4c)FT-IR Spectra of 3p-Br doped with V3 and R3

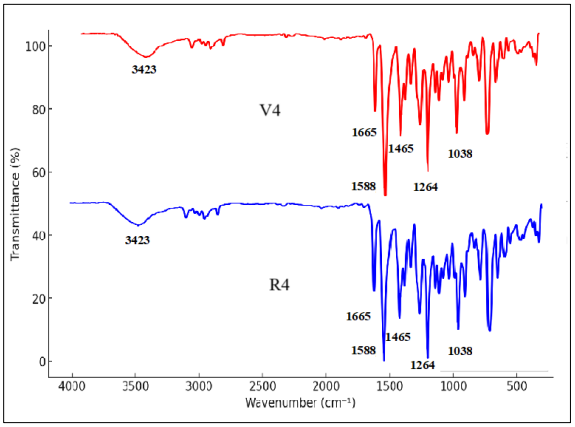


Figure (4d)FT-IR Spectra of 3p-Br doped with V4 and R4

Specific electronic transitions such as π to π* or n to π* transitions. After extracting the energy gap E=1240/nm, it was found that the energy gap of pure 3p-Br is 1.425 eV, which means that the material is a semiconductor and is similar to materials with similar energy gaps such as selenium, silicon carbide, and cadmium selenide which are common in solar cell, laser, and light emitting diodes applications.[10]. The corresponding wavelength is approximately 870 nm, which was extracted from the scheme (2). This means that the material absorbs or emits light in the deep red range of the visible spectrum near the infrared.

The photoluminescence (PL)

Scheme (3), and (4) of the photoluminescence (PL) curve of CV-doped 3p-Br and Rhodamine 6G, respectively, at multiple wavelengths. It is shown that when the 3p-Br complex was doped with the two dyes, phenyl crystal and Rhodamine 6G, this affected the energy gap, which led to the stabilization of the new energy levels within the original energy gap, which effectively reduced the energy difference required for electronic transition, as the emission properties were modified by introducing the two dyes, which led to improving the absorption at the longest wavelengths, and thus

changing the mechanism of electronic transfer to be a resonance energy transfer phenomenon or creating complex states that lead to new electronic transitions.[11] .

UV-VIS Diffuse Reflectance Special (DRS)

Schemes (5), and (6) show the DRS spectrum in strong absorption peaks in the ultraviolet region at a wavelength of about 280 nm, while the 3p-Br compound doped with Rhodamine dye showed a band at a wavelength of about 270 nm. The wavelength is then converted to the electron volt energy gap according to equation (1).

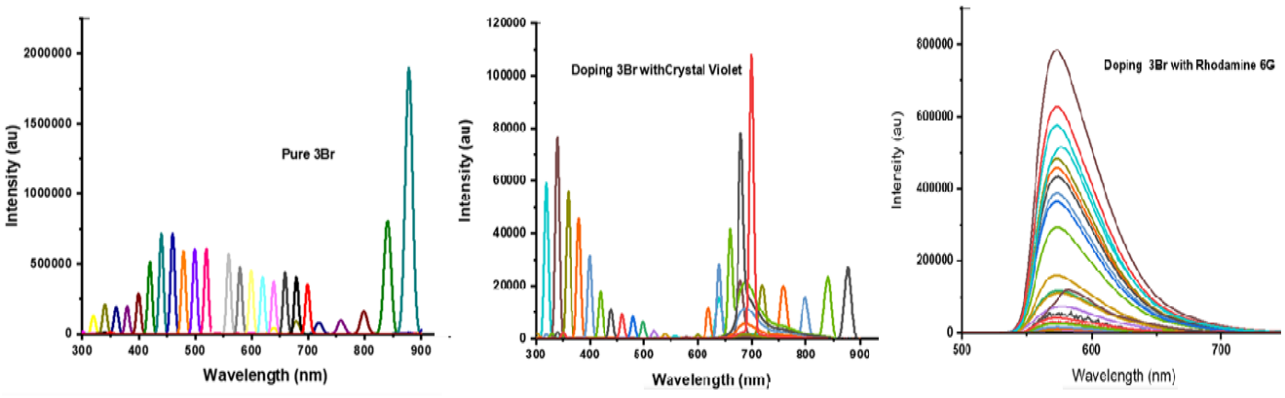
$$E = h\upsilon = 1240/\lambda \qquad (1)$$

1240 is the result of (hc) where (c) is the speed of light, and (h) is the Planck constant when converting the nanometer to the electron volt.

Where $(\alpha\ h\upsilon)^{n}$ is drawn against hu, as n depends on the type of transition; if it is direct, n = 2, and if it is indirect, n = 1/2.[12]

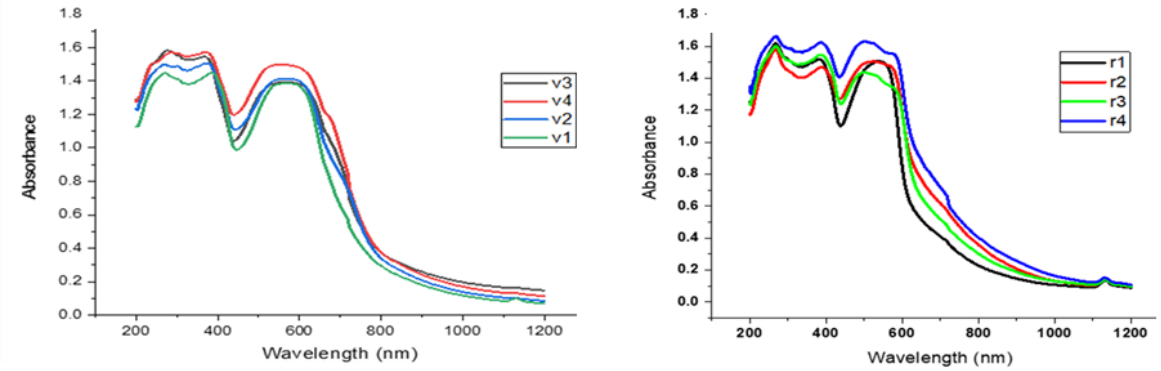
Schemes from (7) to (10) and the plots from (11) to (14) are curves of $(\alpha h\upsilon)^{1/2}$, and $(\alpha h\upsilon)^{2}$ versus photon energy for the compound 3p-Br doped with rhodamine 6G. Schemes from (15) to (18) and the plots from (19) to (22) are curves of $(\alpha h\upsilon)^{1/2}$ [12], and $(\alpha h\upsilon)^{2}$ versus photon energy for the compound 3p-Br doped with crystal violet. Two straight lines can be seen in these resulting curves after drawing the Tauck plot, which shows the Tauck plots when doped with vinyl crystal dye and when doped with rhodamine 6 G dye. It became clear that the value of the energy gap changes with the change in the dye concentration and the value of the energy gap increases when the concentration decreases as in Tables (3),(4),(5), and (6). The change was very large, which means that there is an inverse relationship between the

concentration and the energy gap, which indicates that when semiconductors are doped with other materials, many of their properties and characteristics change and produce new properties that differ relatively from the properties of pure semiconductors, which is what was observed in this study.



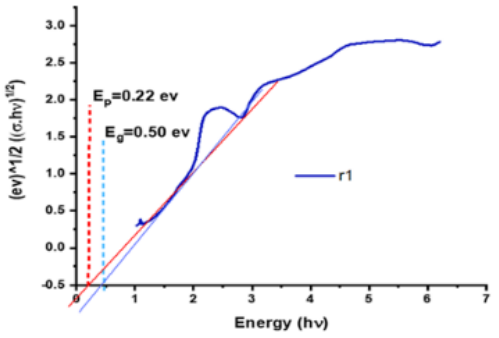
2 3 4

Schemes (2), (3), and (4) show the PL curve of pure 3p-Br and CV-doped R6G at various wavelengths, respectively.

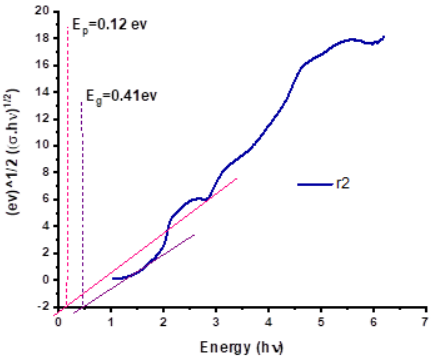


5 6

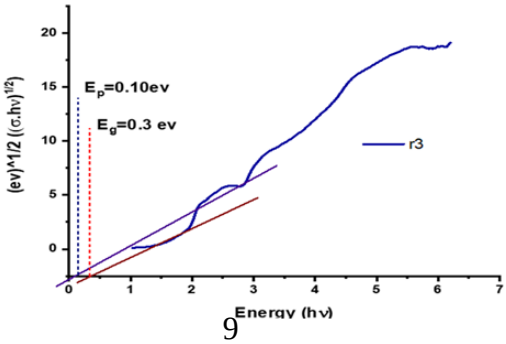
Scheme (5), and (6) The DRS curve of 3p-Br doped with CV, and R6G at various wavelengths, respectively.



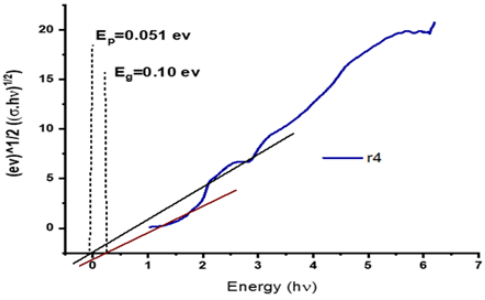
7



8



9

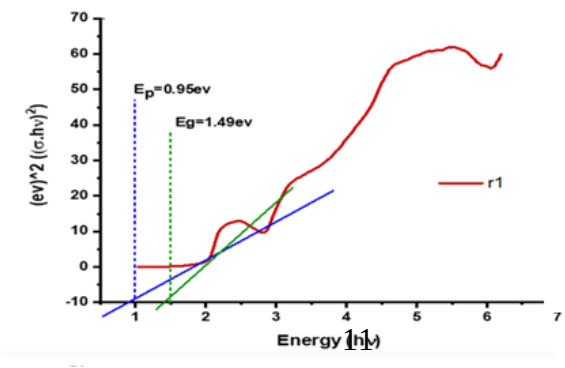


10

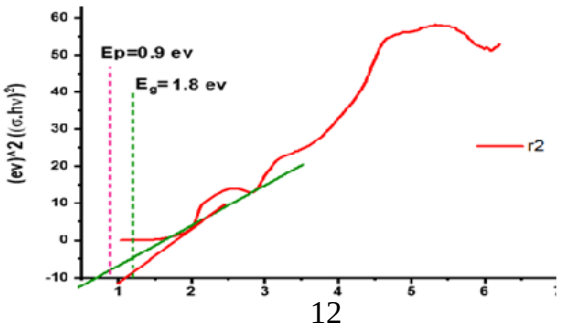
Scheme (7)-(10) The Thuc equation graph shows the gap energy and the photon energy in indirect transmission of 3p-Br doped with R6G 1-4.

Table (2) Relationship gap's energy Doping ratio of R6G in indirect transition

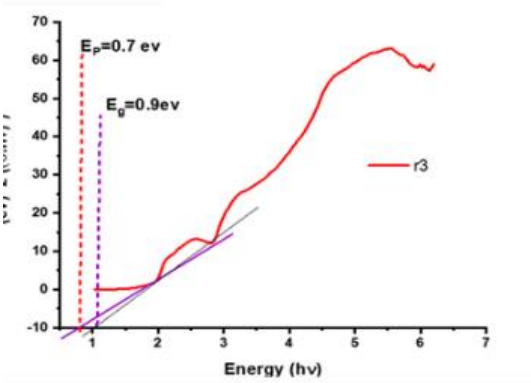
Doping ratio% of Rhodamine 6G	$E_{g\ ind.}$ Ev	$E_{p\ ind.}$ Ev
0.00 (r_0)	1.40	0
0.02 (r1)	0.49	0.22
0.05 (r2)	0.41	0.12
0.07 (r3)	0.30	0.10
0.1 (r4)	0.10	0.05



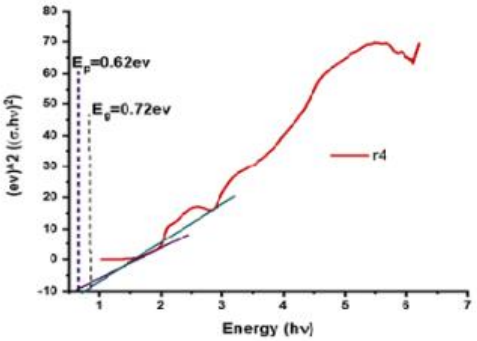
11



12



13

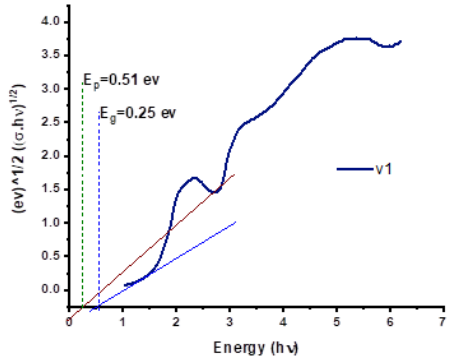


14

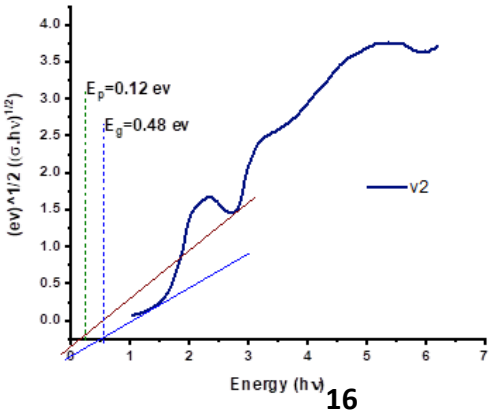
Schemes (11)- (14) The Tauc Plot graph shows the gap energy and the photon energy in direct transmission of 3p-Br doped with r1,r2,r3, and r4.

Table (3) Relationship gap's energy Doping ratio of R6G indirect transition.

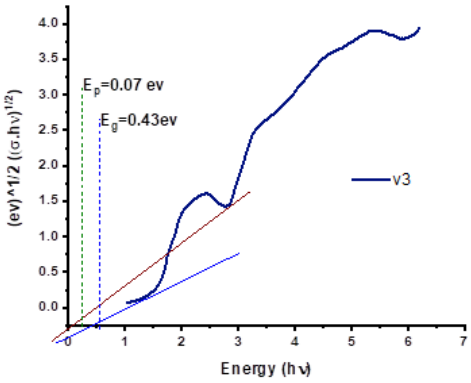
Doping ratio% of Rhodamine 6G	$E_{g\,(dir.)}$ ev	E_p ev
0.00 (r0)	1.40	0
0.02 (r1)	1.40	0.95
0.05 (r2)	1.20	0.90
0.07 (r3)	0.90	0.70
0.1 (r4)	0.72	0.62



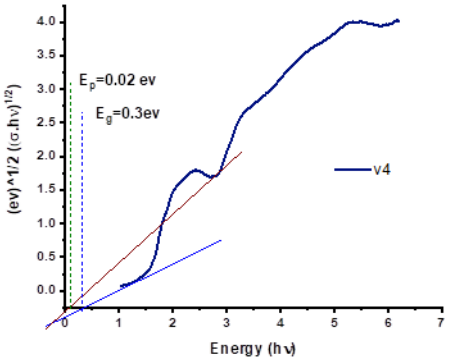
15



16



17

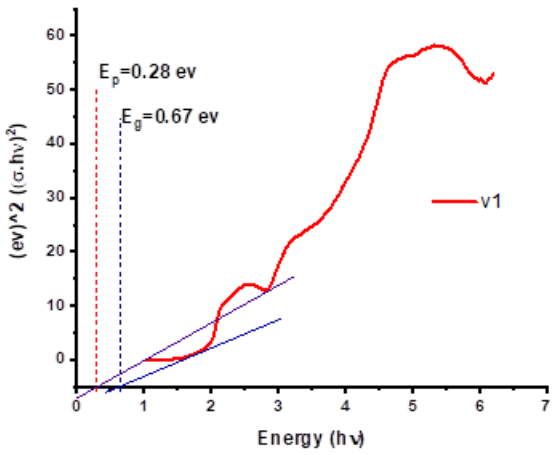


18

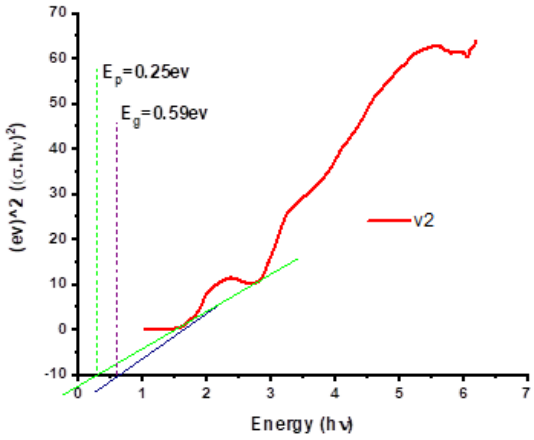
Schemes (15)- (18) The Tauc equation graph shows the gap energy and the photon energy in the indirect transmission of 3p-Br doped with v1,v2,v3, and v4.

Table (4) Relationship gap's energy Doping ratio of CV in indirect transition

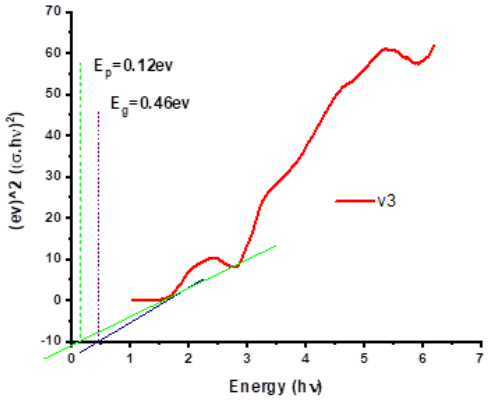
Doping ratio of Crestal Violate	E.g. (indr.) ev	Ep ev
0.00 (v0)	1.5	0.0
0.02 (v1)	0.51	0.25
0.05 (v2)	0.48	0.12
0.07 (v3)	0.43	0.07
0.1 (v4)	0.30	0.02



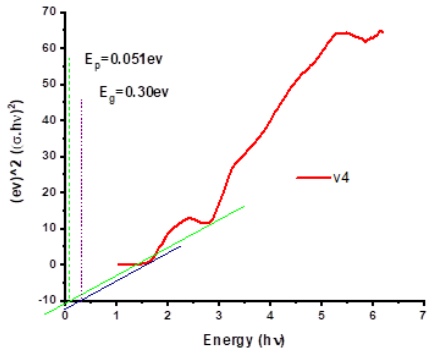
19



20



21



2

Schemes (19) - (22) The Tauc equation graph shows the gap energy and the photon energy in the direct transmission of 3p-Br doped with v1,v2,v3, and v4.

Table (5) Relationship gap's energy with a doping ratio of R6G in direct transition

Doping ratio of Crestal Violate	E.g. (dir.) ev	E_p Ev
0.00 (v_0)	1.50	0
0.02 (v1)	0.67	0.28
0.05 (v2)	0.59	0.25
0.07 (v3)	0.46	0.12
0.1 (v4)	0.30	0.051

Conclusion

This study proposed the preparation of a beta-aminocarbonyl compound, and its physical properties were studied, and it was proven that it behaves as a semiconductor. We doped it with two dyes, namely rhodamine 6G and phenyl crystal, to study the effect of increasing the doping concentration on the band gap and thus on the conductivity. This was proven by conducting FTIR, PL, and DRS spectroscopy, and it was proven that increasing concentration leads to a decrease in the band gap.

Reference

[1] 1. Terna AD, Elemike EE, Mbonu JI, Osafile OE, Ezeani RO. The future of semiconductors nanoparticles: Synthesis, properties, and applications. *Materials Science and* Engineering*: B.* 2021;272:115363.

[2] 2. https://www.sciencefacts.net/band-theory.html.

[3] 3. Brütting W. Introduction to the physics of organic semiconductors. *Physics of organic semiconductors.* 2005:1-14.
[4] 4. Berger LI. *Semiconductor materials.* CRC Press; 2020.
[5] 5. Al-Shamsi Hanan F. Al-Amood H, Hayat H. Abbas,, Al-Tamimi wH. *BasJVetRes.* 2019;18(2):359-375.
[6] 6. Al-Amood H, Al-Hadithi HT, Fadhil F. Structure—Antimicrobial Activity Relationship Investigation of Some Butadiene and Chalcone Derivatives. *J Life Sci.* 2013;7:705-711.
[7] 7. Kadhim SH, Al-Najar AA, Al-Mowali AH. . *European Journal of Material Sciences.* 2016;3(3):1-11.
[8] 8. El Naeem GA, Abd-Elhamid A, Farahat OO, El-Bardan AA, Soliman HM, Nayl A. Adsorption of crystal violet and methylene blue dyes using a cellulose-based adsorbent from sugarcane bagasse: characterization, kinetic and isotherm studies. *Journal of Materials research and technology.* 2022;19:3241-3254.
[9] 9. Douba H, Mohammedi O, Cheknane B. Adsorption of rhodamine 6G dye onto Al-MCM-41 and MCM-41 mesoporous materials. *Kemija u industriji: Časopis kemičara i kemijskih inženjera Hrvatske.* 2022;71(9-10):569-582.
[10] 10. Morab S, Sundaram MM, Pivrikas A. Review on charge carrier transport in inorganic and organic semiconductors. *Coatings.* 2023;13(9):1657.
[11] 11. Cabello-Guzmán G, Seguel M, Fernández L, et al. A photochemical approach to the synthesis of ZnO/CuO films and their application to the photocatalytic degradation of rhodamines (Rh-B and Rh-6G) under UV–Vis light irradiation. *Inorganic Chemistry Communications.* 2023;152:110695.
[12] 12. Haryński Ł, Olejnik A, Grochowska K, Siuzdak K. A facile method for Tauc exponent and corresponding electronic transitions determination in semiconductors directly from UV–Vis spectroscopy data. *Optical Materials.* 2022;127:112205.