



# Synthesis and Structural Study of the Ion-Associates of Sildenafil Citrate with Chromotropic Acid Azo Dyes

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**Keywords:** sildenafil citrate, chromotropic acid azo dyes, Vis spectrophotometry, IR spectra.

Five ion-associates of the drug sildenafil citrate (SC) with mono-chromotropic acid azo dyes, chromotrope 2B (I) and chromotrope 2R (II), and chromotropic acid bi-azo dyes, bis-3,6-(*o*-hydroxyphenylazo)-chromotropic acid (III), bis-3,6-(*p*-N,N-dimethylphenylazo)-chromotropic acid (IV) and 3-phenylazo-6-*o*-hydroxyphenylazo-chromotropic acid (V) have been synthesized. Structural characterization of these novel sildenafil citrate ion-associates was carried out using elemental analysis and spectral techniques (VIS and IR). IR absorption spectra of the investigated ion-associates are studied and compared with those of the pure azo dyes and the drug. The spectral characteristics, oscillator strengths, transition dipole moments and resonance energy of the ion-associates in the ground state have also been calculated.

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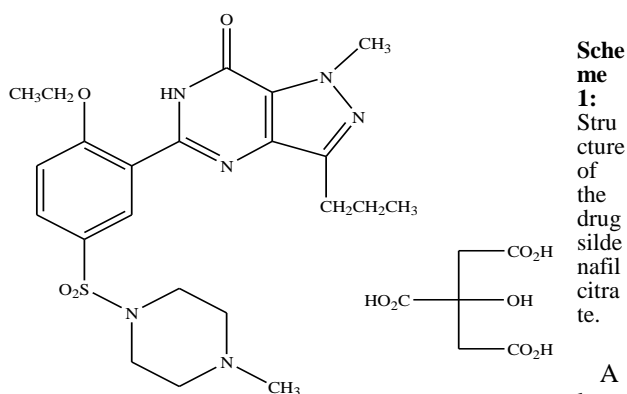
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## Introduction

Sildenafil citrate is designated chemically as 1-[[3-(6,7-dihydro-1-methyl-7-oxo-3-propyl-1H-pyrazolo[4,3-d]pyrimidin-5-yl)-4-ethoxyphenyl]sulfonyl]-4-methylpiperazine citrate [CAS 139755-83-2] and has the structure shown as Scheme 1. Sildenafil citrate is a compound of the pyrazolo-pyrimidinylmethylpiperazine class. It is a selective inhibitor of cyclic guanosine monophosphate (cGMP)-specific phosphodiesterase inhibitors type 5 (PDE5).<sup>1</sup> Singh et al.<sup>2</sup> reviewed and generalized strategies for characterizing adulteration of PDE-5 inhibitors drugs (sildenafil, vardenafil and tadalafil) by using modern, sensitive and selective analytical techniques such as, liquid chromatography with tandem mass spectrometry, Fourier transform (FT) with near infrared spectrometry, and FT with Raman spectrometry. Structure elucidation of a novel synthetic thiono analogue of sildenafil<sup>3</sup> detected in an alleged herbal aphrodisiac was established using LC-MS, UV and IR spectroscopy, MS, and NMR. Kim et al.<sup>4</sup> synthesized new sildenafil analogues containing an ether ring fused into the phenyl ring.



others analogues of sildenafil, including homosildenafil,<sup>5-8</sup> hydroxyhomosildenafil,<sup>7,8</sup> acetildenafil,<sup>7-10</sup> hydroxyacetildenafil<sup>11</sup> and methisosildenafil,<sup>12</sup> have been detected in dietary supplements. Sildenafil citrate (Viagra)

and sildenafil base in pure form are easily and unequivocally characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopy.<sup>13</sup> Two molecularly imprinted polymers (MIPs) as selective sorbents for the solid-phase extraction of sildenafil and its principal metabolite, desmethylsildenafil, were synthesised<sup>14</sup>, using structural analogues of sildenafil as templates.

Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid) is used for preparation of azo dyes which are well known indicators for spectrophotometric determination of metal ions.<sup>15,16</sup> The synthesis and structural study of azo dyes and their complexes was the subject of many new researches.<sup>17-20</sup> The IR spectra of azo dyes were investigated,<sup>21,22</sup> these studies were mainly concerned with the N=N band assignment. Abdel-Ghani et al.<sup>23</sup> presented potentiometric, IR and thermal conductimetric studies on chelates of chromotropic acid with some transition metals. Some azo dyes and their metal complexes were characterized by multinuclear NMR.<sup>24</sup>

In the present study, elemental analysis, electronic and vibrational analyses were applied to investigate the structure of the prepared sildenafil citrate ion-associates with some chromotropic acid azo dyes.

## Experimental

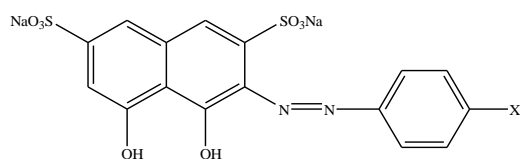
### Instrumentation

Shimadzu FTIR spectrophotometer was used to record IR spectra (on KBr) in the range of 400–4000 cm<sup>-1</sup>. The UV-VIS spectrophotometer model 22 Labomed was used for all spectrophotometric measurements. Elemental analyses were carried out using automatic CHN analyzer (Perkin-Elmer model 2400) at the Microanalytical Center, Faculty of Science, Cairo University.

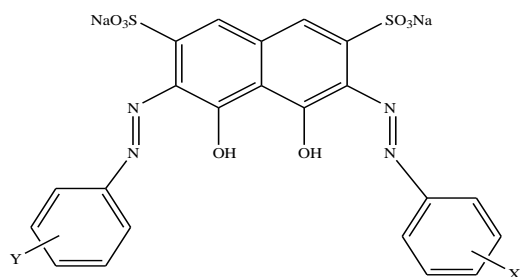
### Reagents

All chemicals used were of the analytical reagent grade. sildenafil citrate was a product of Alkan Pharmaceutical Industries, Cairo, Egypt. Chromotrope 2B (I) and

chromotrope 2R (II) were obtained from Sigma (USA); their structure is shown in Scheme 2. Bi-chromotropic acid azo dyes (III-V) were prepared by diazotization of the corresponding amines with chromotropic acid.<sup>25</sup> The resulting precipitate was re-crystallized<sup>26</sup> (Scheme 3).



**Scheme 2:** Structure of mono-chromotropic acid azo dyes.



**Scheme 3:** Structure of bi-chromotropic acid azo dyes.

## Synthesis

The new solid ion-associates of SC with mono- and bi-azo dyes of chromotropic acid were prepared; 0.1 mmol (0.0513 g of (I), 0.0468 g of (II), 0.0604 g of (III), 0.0658 g of (IV) and 0.0588 g of (V)) were dissolved in about 30 mL methanol and added to 0.2 mmol (0.1332 g) and 0.1 mmol (0.0666 g) of the drug SC for preparation of solid ion-associates of SC with mono-azo (I and II) and bi-azo (III-V) dyes of chromotropic acid, respectively, the drug SC was dissolved in 30 mL of the same solvent. The dye solutions were added slowly to the individual SC solutions with constant stirring. The resulting mixtures were subjected to vigorous stirring, and then the mixture was left until the complete solvent vaporization. The resulting precipitates were filtered, washed thoroughly with petroleum ether and then dried at the room temperature to have fine powder. The structures of the precipitates were determined by elemental analysis, IR and Vis measurements.

## Results and discussion

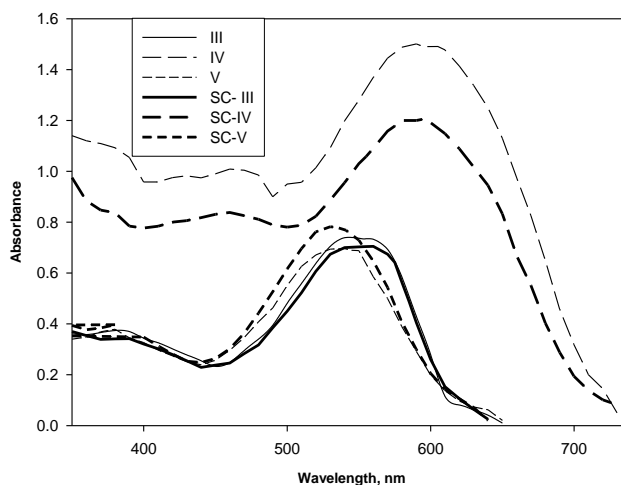
### Microanalysis of SC Solid ion-associates

Table 1 contains the elemental analysis results of the chromotropic acid azo dyes (I-V) ion-associates with the investigated drug (SC). It is noteworthy to mention that the found values of the different elements are in good agreement with the calculated values according to the proposed molecular formulae of the ion-associate. The obtained data reveal that the SC-I and SC-II ion-associates are formed in a

ratio of 2:1 (drug:dye) with a molecular formula of 2SC-(I-II).  $n\text{H}_2\text{O}$ , while SC-(III-V) ion-associates are formed in a ratio of 1:1 (drug:dye) with a molecular formula SC-(III-V).  $n\text{H}_2\text{O}$ , where n is the number of water molecules.

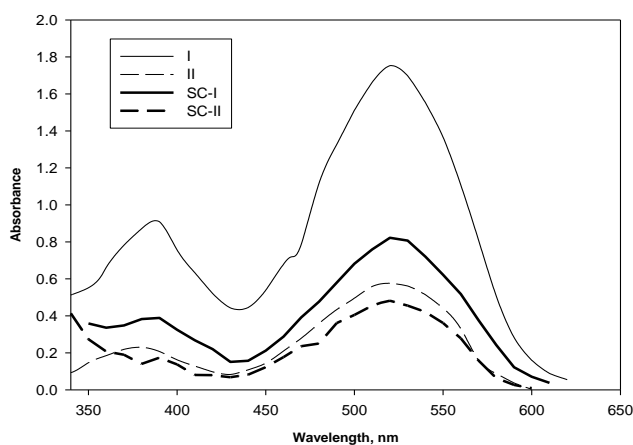
### Visible Spectra of SC Solid ion-associates

The absorption spectra of the azo dyes (I-V) under investigation and also their resulting solid ion-associates with the drug SC were studied against dimethylformamide (DMF) blank. The present spectral measurements were confined to the visible region within the wavelength range 300-600 nm (Figs. 1, 2) using DMF as solvent. The absorption maxima and the molar absorptivities of the azo dyes and their corresponding solid ion-associates are recorded in table 2. The small shift in the absorption maxima and variation in the molar absorptivities values for the reaction products relative to those of pure azo dyes is an indication for the formation of the new ion-associate



compounds.

**Figure 1.** Absorption spectra of the reagents I and II III-V and their corresponding ion- in DMF solvent



**Figure 2.** Absorption spectra of the reagents corresponding ion- and their associates with SC pairs with SC in DMF solvent.

**Table 1:** Data of elemental analysis of the investigated SC ion-associates.

Ion-associate	Chemical formulae	Colour of precipitate	Found (Calc.)			
			C%	H%	S%	N%
SC-I	C <sub>38</sub> H <sub>39</sub> N <sub>9</sub> O <sub>14</sub> S <sub>3</sub> . 10H <sub>2</sub> O	Red	45.72 (45.56)	5.27 (4.26)	7.36 (7.91)	9.97 (11.44)
SC-II	C <sub>38</sub> H <sub>40</sub> N <sub>9</sub> O <sub>14</sub> S <sub>3</sub> . 10H <sub>2</sub> O	Pink	42.69 (45.77)	5.46 (4.49)	7.64 (8.14)	9.98 (11.40)
SC-III	C <sub>44</sub> H <sub>45</sub> N <sub>10</sub> O <sub>14</sub> S <sub>3</sub> Na. 8H <sub>2</sub> O	Black	44.96 (43.99)	4.50 (5.07)	7.50 (8.00)	9.91 (11.05)
SC-IV	C <sub>48</sub> H <sub>54</sub> N <sub>12</sub> O <sub>12</sub> S <sub>3</sub> Na. 12H <sub>2</sub> O	Dark violet	41.90 (43.47)	5.10 (5.80)	6.47 (7.25)	10.04 (12.06)
SC-V	C <sub>44</sub> H <sub>44</sub> N <sub>10</sub> O <sub>13</sub> S <sub>3</sub> Na. 6H <sub>2</sub> O	Black	43.55 (46.00)	4.50 (4.87)	7.36 (8.37)	9.18 (11.10)

### Infrared Spectra

The infrared spectra (IR) of sildenafil citrate (SC) and some of the studied reagents (I-V) and their ion-associates were recorded in the range 4000-400 cm<sup>-1</sup> using KBr discs. Table 3 shows the IR band assignment of the investigated SC ion-associates. The main diagnostic bands in SC ion-associates are assigned in the following discussion. The IR spectra are represented in Figs. 3 and 4.

**Table 2:** Absorption spectral data of the investigated chromotropic acid azo dyes and their ion-associates with SC

	$\lambda_{\max}$ (nm)	$\epsilon_{\max} \times 10^3, \text{L mol}^{-1} \text{cm}^{-1}$
I	515	12.27
I-SC	520	10.93
II	520	2.99
II-SC	520	4.88
III	540	12.40
III-SC	560	11.37
IV	580	21.10
IV-SC	595	10.80
V	540	11.37
V-SC	530	18.04

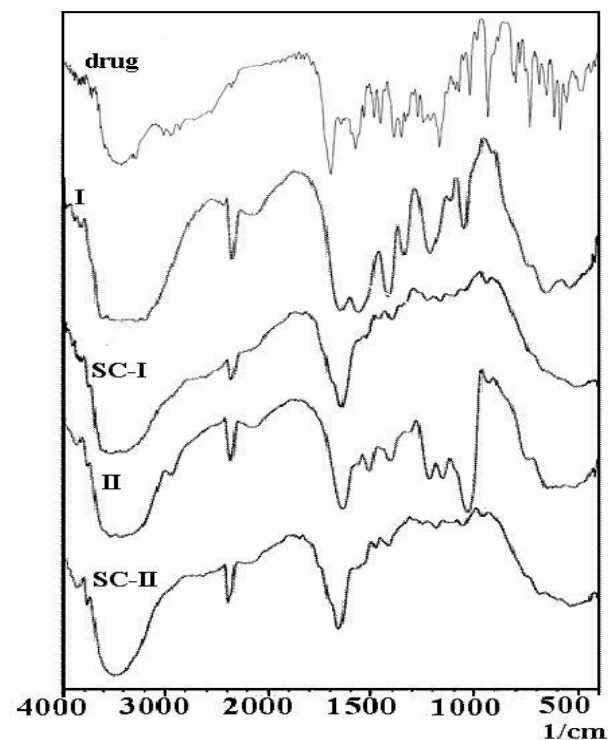
#### Hydroxyl bands

The infrared spectra of the chromotropic acid azo dyes and their ion-associates with SC show a broad hydroxyl group band. The intensity of this band is considerably greater than that of the free OH-vibration frequency. The broad shape can be attributed to the fact that the OH group is involved in hydrogen bonding. One of the two OH groups of chromotropic acid can form an intramolecular hydrogen bond with the azo group while the other one forms an intermolecular hydrogen bond with the oxygen of the  $\alpha$ -OH- group.<sup>27</sup> The band is slightly affected by the nature and position of the substituent (Table 3). There is another absorption band also in the lower frequency region which attributed to OH- deformation occurs around 1100 cm<sup>-1</sup>.

#### Absorption in the 1700–1400 cm<sup>-1</sup> region

This is the region of interest, since it involves bands due to C=O, C=N, C=C, and N=N. The IR-spectra of the drug SC shows two bands at 1701 and 1615 cm<sup>-1</sup>, these bands are assigned to the carbonyl group C=O<sup>28</sup> and vibration of C=N. These bands are shifted to lower or higher frequencies in the IR-spectra of the SC-(I-V) ion-associates, which indicate the formation of new ion-associate between the drug and the investigated azo dyes.

The IR-spectra of the compounds show bands near 1690, 1600 and 1500 cm<sup>-1</sup>. These bands are due to skeletal stretching vibrations C=C. The position of the bands is influenced to a small extent by the nature of substituent groups. However, they depend on a rather greater degree, on the way in which the latter are arranged around the ring. The vibration due to the azo link (N=N) of chromotropic acid azo dyes<sup>27</sup> differ than that of their ion-associates indicating that it has been affected by the reaction with SC.

**Figure 3.** IR spectra of the drug sildenafil citrate and reagents I and II and their ion-associates with the drug (SC-I and SC-II)

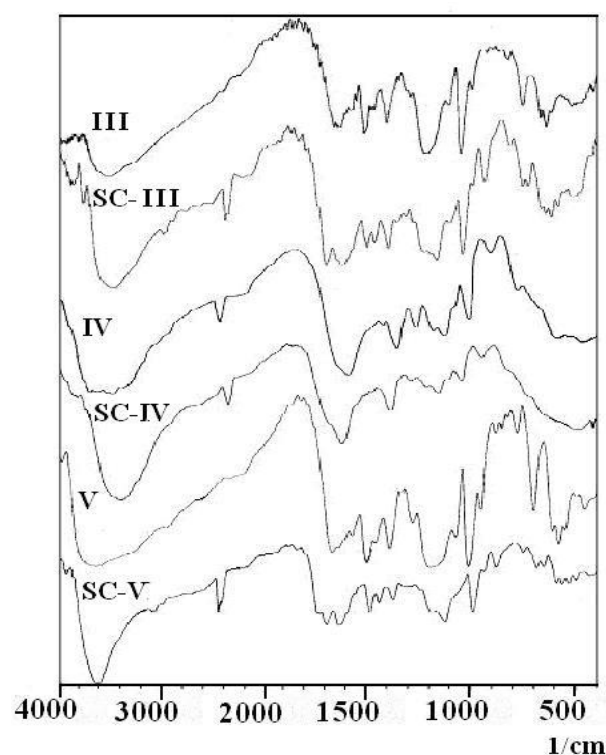
#### Absorption in the 1400–600 cm<sup>-1</sup> Region

This region involves other bands such as C–N stretching vibration, C–O stretching vibration and the aromatic C–H out of plane deformation.<sup>29</sup> C–N and C–O stretching vibration bands are found around 1300 and 1200 cm<sup>-1</sup>, respectively. Their positions vary considerably with structural effects. The vibration bands assigned to the aromatic C–H out of plane deformation are observed near 990 cm<sup>-1</sup>. The IR-spectra of chromotropic acid azo dyes indicate that the sulphonic acid group absorbs within the range 1190-1212 cm<sup>-1</sup> (broad) and 1037-1045 cm<sup>-1</sup> (strong or medium) with a third band around 640 cm<sup>-1</sup>.<sup>27</sup>

**Table 3.** Assignment of IR bands of SC and its ion-associates with the investigated chromotropic acid azo dyes.

SC	I	SC-I	II	SC-II	III	SC-III	IV	SC-IV	V	SC-V	Vibrational assignment
3398 <sup>b</sup>	3190 <sup>b</sup>	3244 <sup>b</sup>	3325 <sup>b</sup>	3414 <sup>b</sup>	3445 <sup>b</sup>	3425 <sup>b</sup>	3372 <sup>b</sup>	3440 <sup>b</sup>	3425 <sup>b</sup>	3425 <sup>b</sup>	νOH
1701 <sup>s</sup>	-	1639 <sup>b</sup>	-	1639 <sup>b</sup>	-	1693 <sup>w</sup>	-	1635 <sup>b</sup>	-	1693 <sup>w</sup>	νC=O
-	1643 <sup>w</sup>	1639 <sup>b</sup>	1639 <sup>m</sup>	1639 <sup>s</sup>	1628 <sup>w</sup>	1693 <sup>w</sup>	1601 <sup>b</sup>	1636 <sup>b</sup>	1620 <sup>w</sup>	1616 <sup>w</sup>	νC=C skeletal vib.
1539 <sup>w</sup>	1558 <sup>w</sup>	-	1566 <sup>w</sup>	1558 <sup>w</sup>	1566 <sup>w</sup>	1643 <sup>w</sup>	-	-	1570 <sup>w</sup>	-	νC=C skeletal vib.
1581 <sup>m</sup>	-	1523 <sup>w</sup>	1504 <sup>w</sup>	-	1500 <sup>w</sup>	1500 <sup>w</sup>	-	-	1508 <sup>m</sup>	1497 <sup>w</sup>	νC=C skeletal vib.
1651 <sup>w</sup>	-	1639 <sup>b</sup>	-	1639 <sup>b</sup>	-	1616 <sup>w</sup>	-	1636 <sup>b</sup>	-	1643 <sup>w</sup>	νC=N
-	1416 <sup>m</sup>	1404 <sup>w</sup>	1404 <sup>w</sup>	1462 <sup>w</sup>	1474 <sup>w</sup>	1462 <sup>w</sup>	1435 <sup>w</sup>	1393 <sup>w</sup>	1400 <sup>m</sup>	1462 <sup>w</sup>	νN=N
1338 <sup>w</sup>	1338 <sup>m</sup>	1354 <sup>w</sup>	1312 <sup>w</sup>	1400 <sup>w</sup>	1396 <sup>m</sup>	1357 <sup>w</sup>	1377 <sup>m</sup>	1392 <sup>m</sup>	1296 <sup>w</sup>	1396 <sup>w</sup>	νC-N
-	1211 <sup>s</sup>	-	1219 <sup>b</sup>	-	1215 <sup>b</sup>	-	1284 <sup>m</sup>	-	1219 <sup>b</sup>	-	νSO <sub>3</sub> <sup>-</sup>
1219 <sup>w</sup>	1211 <sup>s</sup>	1164 <sup>w</sup>	1218 <sup>w</sup>	1165 <sup>w</sup>	1215 <sup>b</sup>	1165 <sup>w</sup>	-	1158 <sup>w</sup>	1219 <sup>w</sup>	1165 <sup>w</sup>	νC-O
-	1041 <sup>s</sup>	1045 <sup>w</sup>	1038 <sup>s</sup>	1038 <sup>w</sup>	1045 <sup>s</sup>	1042 <sup>s</sup>	1042 <sup>s</sup>	1041 <sup>w</sup>	1045 <sup>s</sup>	1042 <sup>s</sup>	νSO <sub>3</sub> <sup>-</sup>
-	665 <sup>m</sup>	-	-	-	640 <sup>w</sup>	-	-	-	640 <sup>w</sup>	-	vibrations due to SO <sub>3</sub> <sup>-</sup>
941 <sup>s</sup>	-	937 <sup>w</sup>	-	-	-	995 <sup>w</sup>	-	933 <sup>m</sup>	-	991 <sup>w</sup>	δC-H out-of-plan def.

b: broad, s: strong, m: medium and w: weak.



**Figure 4.** IR spectra of reagent III-V and their ion-pairs with sildenafil citrate.

#### Spectral Characteristics of the Solid ion-associates

The oscillator strength ( $f$ ), which is a dimensionless quantity used to express the transition probability of the complex band<sup>30</sup>, and the transition dipole moment ( $\mu_{EN}$ ) of the ion-associate complexes<sup>31</sup> were calculated from the following equations:

$$f = 4.32 \times 10^{-9} [\epsilon_{\max} \Delta\nu_{1/2}] \quad (1)$$

$$\mu = 0.0958 \left[ \frac{\epsilon_{\max} \Delta\nu_{1/2}}{\nu_{\max}} \right]^{1/2} \quad (2)$$

where  $\Delta\nu_{1/2}$  is the band width of the absorption peak at its half height,  $\epsilon_{\max}$  and  $\nu_{\max}$  are the extinction coefficient (molar absorptivity) and the wave number at the maximum absorption of the ion-associate, respectively. In these equations,  $\nu$  has been expressed in  $\text{cm}^{-1}$  unit. Results are shown in Table 4. The relative low values of  $f$  indicate a weak interaction between the cation–anion pairs.<sup>32</sup> The  $R_N$  is the resonance energy of the ion-associate in the ground state, which is obviously a contributing factor to the stability constant of the ion-associate (a ground state property), can be determined by following equation.<sup>33</sup>

$$\epsilon_{\max} = \frac{7.7 \times 10^4 |R_N|}{h\nu_c} - 3.5 \quad (3)$$

where  $\nu_c$  is the frequency of the absorption band of the ion-associate at maximum absorption. Resonance energies for the SC ion-associates with different chromotropic acid azo dyes are given in Table 4.

#### Conclusion

A new class of sildenafil citrate ion-associate compounds with chromotropic acid azo dyes has been synthesized and characterized. The results obtained in the present study showed that, the elemental analysis values of C, H, N and S are in good agreement with the calculated values according to the proposed molecular formulae of the ion-associates. The small shift in the absorption maxima ( $\lambda_{\max}$ ) in the VIS spectra and the change in the molar absorptivity values of the solid ion-associates relative to those of pure azo dyes reveal the formation of new ion-associates. This, also, was confirmed by the change in the position of the IR spectral bands of the prepared solid ion-associate compounds.

**Table 4:** The UV-spectral properties of the solid ion-associates of sildenafil citrate with reagents (I-V), absorption maxima ( $\lambda_{\max}$ ), transition energy ( $h\nu_{\max}$ ), molar absorptivity ( $\epsilon$ ), oscillator strength ( $f$ ), transition dipole moment ( $\mu_{\text{EN}}$ ), resonance energy (RN) and wave number of maximum absorption ( $\nu_{\max}$ ).

Parameter	Reagent				
	I	II	III	IV	V
$\lambda_{\max}$ (nm)	520	520	560	595	530
$h\nu_{\max}$ (eV)	3.82	3.82	3.55	3.34	3.75
$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	10.93 x10 <sup>3</sup>	4.88x10 <sup>3</sup>	11.37x10 <sup>3</sup>	8.10x10 <sup>3</sup>	18.07x10 <sup>3</sup>
$f$	4.72 x10 <sup>-10</sup>	1.83 x10 <sup>-10</sup>	5.40x10 <sup>-10</sup>	4.54x10 <sup>-10</sup>	8.82x10 <sup>-10</sup>
$\mu_{\text{EN}}$ (Debye)	2.28x10 <sup>-4</sup>	1.42x10 <sup>-4</sup>	2.53x10 <sup>-4</sup>	2.39x10 <sup>-4</sup>	3.15x10 <sup>-4</sup>
RN (eV)	0.362	0.198	0.345	0.268	0.483
$\nu_{\max}$ (cm <sup>-1</sup> )	1.92x10 <sup>4</sup>	1.92x10 <sup>4</sup>	1.78x10 <sup>4</sup>	1.68x10 <sup>4</sup>	1.88x10 <sup>4</sup>

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