Some Aryl-1,2,4-triazol-1-ium Phenacylids in Binary Hydroxyl Solvent Mixtures. Computational and Spectral Study

Dana Ortsana Dorohoi 1, Dan Gheorghe Dimitriu 1,*, Ana Cezarina Morosanu 1,*, Nicoleta Puica Melniciuc 2, Ion Hurjui 3, Mihaela Miron 3, Gabriel Grigore Mariciuc 3, Valentina Closca 4 and Corina Cheptea 5

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Abstract: Four carbanion monosubstituted p-aryl-1,2,4-triazol-1-ium methylids are subjected to a comparative study between their spectral and quantum-mechanical parameters in order to obtain more information about their structural features in hydroxyl solvents as water and ethanol and also on the nature of electronic absorption transitions from the visible range. The quantum mechanical analysis, made by the Spartan’14 program, established a series of molecular parameters of the studied ylids important for their reactivity and for intermolecular interactions with hydroxyl liquids. An extensive solvatochromic study of 1,2,4-triazol-1-ium ylids is impossible due to their limited solubility in liquids. Binary solvent mixtures of water and ethanol with known solvent parameters from the literature were used for this study. The electronic absorption spectra in binary solvents water and ethanol were used to establish the influence of intermolecular interactions on the spectral characteristics of the studied methylids and also on the composition of their first solvation shell in ternary solutions. The difference between the interaction energies in molecular pairs ylid–water and ylid–ethanol was determined based on the statistical cell model applied to the ternary solutions of the type of ylid + water + ethanol. The obtained values are very small due to the hydroxylic nature of the two solvents.

Keywords: p-phenyl-1,2,4-triazol-1-ium phenacylids; p-tolyl-1,2,4-triazol-1-ium phenacylids; electronic absorption spectra; water + ethanol binary solvent; intermolecular interaction energy

1. Introduction

The aromatic compounds are intensively investigated due to their importance in the pharmaceutical industry, where more than half of the known drugs contain at least one heterocyclic compound [1]. The compounds studied in this paper contain triazolium heterocycle and are frequently used in industry and techniques, as established numerous articles [1–9].

Both pharmacological and clinical implications of the triazolium agents have been specified in some reviews [2,3]. Many relatively recent reports [4–8] have analyzed the chemical and biological applications of triazolium ylids and of their derivatives. Besides the multiple applications of the 1,2,4-triazolium derivatives [2–8], the ylids having 1,2,4-
triazolium derivatives as cation [9,10] are known as precursors to obtaining new heterocycle compounds, which are very important in the pharmaceutical industry.

1,2,4-Triazol-1-ium ylids are dipolar and polarizable heterocyclic compounds with opposite charges located near one positive nitrogen belonging to a triazolium ring and near the negative carbon, named carbanion [9,10]. The covalent bond N+−C− is called a ylid bond. In the carbanion monosubstituted p-aryl-1,2,4-triazolium methylid, the carbanion is covalently bonded to one hydrogen atom and to a phenacyl or p-nitro-phenacyl substituent, known as an electronegative atomic group. The higher the carbanion substituent electronegativity, the more stable the ylid is.

Knowledge about the interactions between triazolium ylids and solvent molecules are very useful because the majority of the ylids reactions take place in situ. Some information about the intermolecular interactions from liquid solutions of triazolium ylids have previously been published [11–14] based on spectral studies in the visible range. Both the universal and specific interactions were emphasized in binary and ternary solutions of 1,2,4-triazol-1-ium ylids.

Spectral studies were achieved in a reduced number of solvents, both in protic and aprotic solvents [13–15], due to the reduced solubility of 1,2,4-triazol-1-ium ylids in the majority of liquids. This is the reason why an extensive solvatochromic study of these ylids has not yet been published.

A series of spectral studies in binary hydroxyl liquids with known solvent parameters [16] had as a subject some carbanion monosubstituted triazolium ylids [12–15]. The binary solvents containing two miscible transparent liquids (both solving the spectrally active molecules) offer the possibility of varying the solvent parameters by varying the molar fractions in the liquids’ mixture. The nature and the strength of the intermolecular interactions were established based on the spectral shifts measured in the visible absorption electronic spectra of the triazolium ylids ternary solutions [12,14]. The composition of the ylid first solvation shell and also the difference between the interaction energy between the ylid and hydroxyl molecules were estimated using the statistical cell model of ternary solutions.

In this study, some structural and electro-optical parameters of four carbanion monosubstituted triazolium ylids established by quantum-chemical analysis are correlated with the previously obtained spectral results [14,15]. New information regarding the structural and spectral features of 1,2,4-triazol-1-ium methylid was obtained from this comparison.

2. Materials and Methods

The structures of the studied molecules in this research are schematically specified in Figure 1 and Table 1.

![Figure 1. Schematic formula of the studied 1,2,4-triazol-1-ium ylids.](image-url)
Table 1. Structural formulas for the studied carbanion monosubstituted 1,2,4-triazol-1-ium ylids.

| Ylid     | \( R_1 \)       | \( R_2 \)       | Name                                               |
|----------|------------------|------------------|----------------------------------------------------|
| PTPY     | C<sub>6</sub>H<sub>5</sub> | COC<sub>6</sub>H<sub>5</sub> | 4'-phenyl-1,2,4-triazol-1-ium-phenacylid            |
| PTNPY    | C<sub>6</sub>H<sub>5</sub> | COC<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub> | 4'-phenyl-1,2,4-triazol-1-ium-4-nitro-phenacylid    |
| TTPY     | C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub> | COC<sub>6</sub>H<sub>5</sub> | 4'-toly1-1,2,4-triazol-1-ium-phenacylid             |
| TTNPY    | C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub> | COC<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub> | 4'-toly1-1,2,4-triazol-1-ium-4-nitro-phenacylid     |

The studied substances were prepared by the salt method [9,10]. Their purity was tested by quantitative elemental analysis and by spectral analysis (\(^1\)H nuclear magnetic resonance and Fourier-transform infrared spectra).

Spectrally grade solvent ethanol was sourced from the Merck Company and used without supplementary purification. Bi-distilled water was obtained in our laboratory. The molar fractions of the binary solvent mixtures were realized with a step of 0.05 and the weightings were repeated twice in order to improve the precision, having in mind the very small quantities of the substances. The weighting was made with a balance that had a precision of \(10^{-5}\) g.

Initially, two diluted solutions of one ylid were realized both in water and in ethanol, at the same concentration, \(10^{-4}\) mol/L. Ternary solutions were obtained by mixing the two solutions in various mole fractions with 0.05 steps, as described in [16] for determining Kamlet–Abboud–Taft (KAT) parameters.

The electronic absorption spectra were recorded by the Specord UV Vis Carl Zeiss Jena spectrophotometer with a data acquisition system. The wavenumber in the maximum of the electronic absorption band was estimated based on the first derivative of the electronic spectrum.

The molar concentration of the ylid in solution was very small—about \(10^{-4}\) mol/L. The interactions between the solute molecules are negligible at this molar concentration.

The KAT parameters of the binary solvent mixtures were taken from [16].

The quantum mechanical characterization of the triazolium ylids was performed by using Spartan’14 software [17,18], both for the isolated molecules and for their binary solutions achieved in water and ethanol. The details of the used level of theory are as follows:

- ultrafine pruned integration grid (99,590) was used;
- the requested threshold for root mean square (RMS) change in the density matrix during the self-consistent-field (SCF) procedure was \(10^{-8}\) a.u.;
- the requested convergence criteria for the electronic energies were \(10^{-6}\) Hartree;
- electrostatic charges were obtained by fits to electrostatic potentials;
- the isodensity value adopted to construct the frontier molecular orbitals was 0.032 a.u.;
- the model employed for the solvated molecules was SM8 (implicit solvent);
- the model employed to simulate the excited states was the Time Dependent Density-Functional Theory (TDDFT) algorithm.

3. Results and Discussion

3.1. Quantum Mechanical Results

The quantum mechanical evaluations were made in this study in order to connect them with the spectral results previously obtained [14,15] and revised. The revision demonstrated the accuracy of the previous spectral experiments.

As with the other cycloimmonium ylids [19–21], the 1,2,4-triazol-1-ium ylids were characterized by a zwitterionic covalent bond (ylid bond) between a positive charged nitrogen belonging to triazol-1-ium cycle and the carbanion N\(^+\)-C\(^-\). The amphiphilic nature of the studied ylid was given by the opposite charges located near the component atoms of the ylid bond. The electronic charges near the component atoms in a vacuum state and in water solutions, computed by Spartan’14 programs, are given for each of the studied molecules in Figures 2 and 3.
As with the other cycloimmonium ylids [19–21], the 1,2,4-triazol-1-ium ylids were studied molecules in Figures 2 and 3. These figures illustrate the change in symmetry of the valence electronic orbital (LUMO) for each studied triazolium ylid in a vacuum and in water. The same tendency was also evidenced for ethanol solutions.

The highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) for each studied triazolium ylid in a vacuum and in water are illustrated in Figures 4–7. These figures illustrate the change in symmetry of the valence electronic cloud when transitions between HOMO and LUMO take place, indicating the shift of the electron density in the visible absorption process.

Figures 2 and 3 show that the charge separation on the ylid bond is the highest for PTPY. The presence of p-nitro-phenacyl at the ylid carbanion decreases the charge separation of PTNPY compared with PTPY and increases the charge separation of TTNPY compared with TTPY.

As seen in Figures 2 and 3, the charges separation on the ylid bond $N^+–\text{C}^-$, computed by Spartan 14, increases for all studied ylids when these molecules pass from an isolated state to water solutions. The same tendency was also evidenced for ethanol solutions.

Figure 2. Electronic charges on the component atoms for the optimized structure of the studied ylids: (a) PTPY in isolated state; (b) PTPY in water solution; (c) PTNPY in isolated state; (d) PTNPY in water solution.

Figure 3. Electronic charges on the component atoms for the optimized structure of the studied ylids: (a) TTPY in isolated state; (b) TTPY in water solution; (c) TTNPY in isolated state; (d) TTNPY in water solution.
As seen in Figures 2 and 3, the charges separation on the ylid bond N+–C−, computed by Spartan 14, increases for all studied ylids when these molecules pass from an isolated state to water solutions. The same tendency was also evidenced for ethanol solutions. The highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) for each studied triazolium ylid in a vacuum and in water are illustrated in Figures 4–7. These figures illustrate the change in symmetry of the valence electronic cloud when transitions between HOMO and LUMO take place, indicating the shift of the electron density in the visible absorption process.

Figure 4. (a) HOMO orbitals for isolated PTPY molecule; (b) LUMO orbitals for isolated PTPY molecule; (c) HOMO orbitals for PTPY molecule in water; (d) LUMO orbitals for PTPY molecule in water.

Figure 5. (a) HOMO orbitals for isolated PTNPY molecule; (b) LUMO orbitals for isolated PTNPY molecule; (c) HOMO orbitals for PTNPY molecule in water; (d) LUMO orbitals for PTNPY molecule in water.

The electron distributions in HOMO and LUMO of the studied ylids dissolved in ethanol are similar to those dissolved in water and, consequently, they are not illustrated in Figures 4–7.

From Figure 4 it can be seen that the electron distribution in the excited state of the isolated PTPY molecule (LUMO, Figure 4a) differs from that in the excited state of PTPY in water solution (LUMO, Figure 4b). When it passes from HOMO to LUMO in a vacuum, the electron cloud density of the PTPY molecule is shifted to the phenyl substituent of the heterocycle (Figure 4b), while the electron cloud is dispersed on the entire molecule (Figure 4d) in PTPY water solution when the same transition takes place. While in the vacuum state (isolated molecule), the absorption electronic transition is realized by n–π*
transfer of electrons from the carbanion towards the heterocycle and its substituent (phenyl or tolyl); in water the visible photon absorption induces the dispersion of the valence electron density on the entire molecule.

Figure 6. (a) HOMO orbitals for isolated TTPY molecule; (b) LUMO orbitals for isolated TTPY molecule; (c) HOMO orbitals for TTPY molecule in water; (d) LUMO orbitals for TTPY molecule in water.

Figure 7. (a) HOMO orbitals for isolated TTNPY molecule; (b) LUMO orbitals for isolated TTNPY molecule; (c) HOMO orbitals for TTNPY molecule in water; (d) LUMO orbitals for TTNPY molecule in water.

Some results of quantum mechanical calculations with Spartan’14 are listed in Tables 2–5 for each ylid in the vacuum and in two hydroxyl solvents (water, ethanol). Tables 2–5 refer to the computed molecular parameters containing some molecular parameters influencing the nature of the intermolecular interactions in solutions, such as polarizability, HOMO and LUMO energies, HBA and HBD counts. In Tables 2–5, the
energy values for the first and second vibrational levels of HOMO and LUMO for the studied ylids are written.

**Table 2.** Quantum mechanical parameters of PTPY in vacuum, water and ethanol computed with Density Functional EDF2, 6-31G* from Spartan’14.

| PTPY | Vacuum       | Water       | Ethanol      |
|------|--------------|-------------|--------------|
| Energy (au)    | -856.338    | -856.358    | -856.368     |
| Energy(aq)     | -856.352    | N/A         | N/A          |
| Solvation E (kJ/mol) | -34.96    | N/A         | N/A          |
| E HOMO (eV)    | -4.52; -5.6 | -4.97; -6.2 | -4.90; -6.1  |
| E LUMO (eV)    | -1.43; -1.0 | -1.34; 0.8  | -1.29; -0.8  |
| Dipole Moment (D) | 7.14    | 10.66       | 10.44        |
| Area (Å²)      | 290.87      | 291.96      | 291.92       |
| Volume (Å³)    | 275.96      | 276.35      | 276.32       |
| PSA (Å²)       | 23.370      | 24.057      | 23.938       |
| Ovality        | 1.42        | 1.42        | 1.42         |
| Polarizability (Å³) | 63.03    | 62.93       | 62.93        |
| HBD Count      | 0           | 0           | 0            |
| HBA Count      | 3           | 3           | 3            |

**Table 3.** Quantum mechanical parameters of PTNPY in vacuum, water and ethanol computed with Density Functional EDF2, 6-31G* from Spartan’14.

| PTPY | Vacuum       | Water       | Ethanol      |
|------|--------------|-------------|--------------|
| Energy (au)    | -1060.759    | -1060.782   | -1060.791    |
| Energy(aq)     | -1060.7128   | N/A         | N/A          |
| Solvation E (kJ/mol) | -32.34    | N/A         | N/A          |
| E HOMO (eV)    | -4.85; -6.0  | -5.10; -6.1 | -5.05; -6.3  |
| E LUMO (eV)    | -2.54; 1.15  | -2.88; -1.30 | -2.79; -1.20 |
| Dipole Moment (D) | 13.41    | 18.66       | 18.20        |
| Area (Å²)      | 316.22      | 317.28      | 317.29       |
| Volume (Å³)    | 297.37      | 297.77      | 297.75       |
| PSA (Å²)       | 62.08       | 62.86       | 62.74        |
| Ovality        | 1.47        | 1.47        | 1.47         |
| Polarizability (Å³) | 64.84    | 65.00       | 64.99        |
| HBD Count      | 0           | 0           | 0            |
| HBA Count      | 6           | 6           | 6            |

**Table 4.** Quantum mechanical parameters of TTPY in vacuum, water and ethanol computed with Density Functional EDF2, 6-31G* from Spartan’14.

| PTPY | Vacuum       | Water       | Ethanol      |
|------|--------------|-------------|--------------|
| Energy (au)    | -895.598    | -895.641    | -895.651     |
| Energy(aq)     | -895.617    | N/A         | N/A          |
| Solvation E (kJ/mol) | -50.92    | N/A         | N/A          |
| E HOMO (eV)    | -4.47; -5.50 | -4.96; -6.2 | -4.89; -6.10 |
| E LUMO (eV)    | -1.34; -0.90 | -1.32; -0.90 | -1.27; -0.80 |
| Dipole Moment (D) | 10.54    | 11.22       | 11.01        |
| Area (Å²)      | 314.64      | 311.78      | 311.77       |
| Volume (Å³)    | 295.33      | 294.54      | 294.53       |
| PSA (Å²)       | 25.017      | 24.048      | 23.930       |
| Ovality        | 1.47        | 1.46        | 1.46         |
| Polarizability (Å³) | 64.65    | 64.41       | 64.41        |
| HBD Count      | 0           | 0           | 0            |
| HBA Count      | 3           | 3           | 3            |
Table 5. Quantum mechanical parameters of TTNPY in vacuum, water and ethanol computed with Density Functional EDF2, 6-31G* from Spartan’14.

|                | Vacuum          | Water            | Ethanol          |
|----------------|-----------------|------------------|------------------|
| Energy (au)    | −1100.04229 au  | −1100.06512 au   | −1100.07469 au   |
| Energy(aq) (au)| −1100.054       | N/A              | N/A              |
| Solvation E (kJ/mol) | −30.95           | N/A              | N/A              |
| E HOMO (eV)    | −4.92; −6.0     | −5.09; −6.35     | −5.04; −6.30     |
| E LUMO (eV)    | −2.19; −1.60    | −2.87; −1.30     | −2.78; −1.3      |
| Dipole Moment (D) | 14.08            | 19.19            | 18.72            |
| Area (Å²)      | 336.23          | 337.29           | 337.26           |
| Volume (Å³)    | 315.61          | 315.99           | 315.97           |
| PSA (Å²)       | 62.096          | 62.925           | 62.768           |
| Ovality        | 1.50            | 1.50             | 1.50             |
| Polarizability (Å³) | 66.33          | 66.48            | 66.47            |
| HBD Count      | 0               | 0                | 0                |
| HBA Count      | 6               | 6                | 6                |

The quantum mechanical computations indicate an increase in the dipole moment of the electronic ground state when the PPTY ylid passes through the vacuum into the water solution (from 7.14 D in vacuum to 10.66 D in water solution) as can be seen in Table 2.

By the HBA and HBD counts from Table 2, we can see the basic nature of the studied compounds (HBD = 0) and their ability to participate in hydrogen bonds by accepting protons from the hydroxylic molecules. There are three places in which the protons can be added to the PTPY ylid (HBA = 3).

The energetic values written in these tables can be used for estimating some other molecular characteristics, such as ionization potential, electron affinity, chemical strength and so on [13].

Spatial characteristics (as area, volume or polar surface area (PSA)) listed in Tables 2–5 provide information about the steric interactions between ylid and solvent and also about the ylid ability to penetrate the membrane cells [22]. For example, as shown in Table 2, PTPY is a dipolar and polarizable molecule that is able to penetrate the cell membranes, because its PSA is smaller than 90 Å.

The properties of PTNPY are illustrated in Figure 5 and Table 3.

In the case of PTNPY, the distributions in HOMO and respective LUMO computed in a vacuum and water do not essentially differ (Figure 5a,b), but there are differences in the values of the PTNPY dipole moments for isolated states and for water solutions of this molecule (13.41 D in vacuum and 18.66 D in water solution). The visible photon absorption shifts the valence electron density from the carbanion towards the p-nitrophenacyl substituent of the carbanion (see Figure 5), due to the strong electron withdrawing ability of the nitro group [9,10], both for the isolated molecule and for its water solution.

The parameters computed by Spartan’14 for PTNPY are listed in Table 3. From Table 3 it can be seen that the PTNPY molecule has high polarizability and the ability to penetrate the cell membranes, because its PSA is smaller than 90 Å [22].

When the data in Tables 2 and 3 are compared, one can see the different numbers for HBA counts for the two ylids, PTPY and PTNPY. The atomic group –NO$_2$ adds supplemental possibilities to receive protons from the hydroxyl solvents by PTNPY molecule. So, PTNPY possesses six places, while PTPY has only three places in which the protons from the hydroxyl solvents can be added.

The HOMO and LUMO electron distributions in the TTPY molecule in an isolated state and in water solution are suggested in Figure 6, respectively. The parameters computed by Spartan’14 of the TTPY molecule for a vacuum state and for its solutions in water and ethanol are listed in Table 4.

Figure 6 shows different distributions of the valence electrons in HOMO and LUMO of TTPY in isolated or solution states, due to the presence of the methyl group in para position of the phenyl substituent. The LUMO of TTPY is enriched in electron density on
the heterocycle and its substituent in vacuum (Figure 6, LUMO), while in water solution (Figure 6, LUMO), the LUMO electron density is dispersed on the entire TTPY chemical structure. The ground state dipole moment of TTPY increases from the vacuum state (10.54 D) to water solution (11.22 D), as shown in Table 4.

As in the case of PTPY (see Table 2), TTPY has only three possibilities for adding protons from the hydroxyl molecules (HBA = 3), as shown in Table 4.

TTPY is a dipolar molecule characterized by high polarizability, both in a vacuum and in hydroxyl liquids. The small PSA value of TTPY indicates the ability of this molecule to penetrate cell membranes. In hydroxyl solutions, the PSA values of TTPY decrease, indicating its higher penetrability in cell membranes, compared with that of the isolated molecule.

The electron distribution in HOMO and LUMO of the TTNPY molecule is given in Figure 7 for the isolated molecule and for its water solution.

Figure 7 shows a similitude in the electron distribution in HOMO and LUMO both in a vacuum and in water solutions of TTNPY.

The molecular parameters of TTNPY in a vacuum, water and ethanol are listed in Table 5. The TTNPY dipole moment varies from 14.08 D to 19.19 D when its molecules pass from the vacuum to the water solution. Table 5 shows that TTNPY is a dipolar and polarizable molecule with a suitable value of PSA for the cell membranes’ penetration and with zero HBD counts indicating its basic nature. The HBA counts indicate the numbers of the molecular places at which the proton can be added to the molecule.

From the data presented in Tables 3 and 5 it can be seen that the nitro-phenacylids PTNPY and TTNPY have six HBA counts, compared with PTPY and TTPY which have only three HBA counts. (See Tables 2 and 4).

Using the data referring to the HOMO and LUMO energies from Tables 2–5 (expressed in cm$^{-1}$), the possible visible electron transitions in absorption are shown by arrows in Figures 8 and 9 and they can be compared with the experimental results given in [14,15] and are repeated in our experiments for water and ethanol (see Table 6 in the Spectral Results section).

Let us compare Figures 8 and 9 for the case of the isolated molecules having a common substituent of carbanion, namely phenacyl. The wavenumbers corresponding to HOMO–LUMO transitions are 24,924 cm$^{-1}$ for PTPY and 25,247 cm$^{-1}$ for TTPY in the vacuum state of ylids. When the ylids are dissolved in water, the wavenumbers of the corresponding transitions increase by 4356 cm$^{-1}$ in the case of PTPY and by 4113 cm$^{-1}$ in the case of TTPY. The wavenumbers of the same band also increase when the ylid passes from ethanol to water (see Figures 8 and 9). A blue shift of this band is computed by the Spartan’14 software when the molecules pass from a vacuum to a polar solvent.

The relatively small intensity of this band in the electronic absorption spectrum, its disappearance in an acid medium and the blue shift in the wavenumber scale argue the attribution of this band to an $n$–$\pi^*$ transition. The lone electron pair of the ylid carbanion is involved in this transition [14,15]. From Figures 4b and 6b it can be seen that this band appears by similar restructuration of the valence electron cloud of the two molecules (PTPY and TTPY). In a vacuum (isolated molecule), both for the cases of PTPY and TTPY, the charge transfer transition shifts the electron cloud from the ylid bond towards the heterocycle substituent. In water (Figures 4b and 6b), the visible absorption induces the electron cloud dispersion on the entire molecule, for both PTPY and TTPY (Figures 4d and 6d).

The ylids PTNPY and TTNPY have the same substituents to carbanion and differ by the methyl group attached at the heterocycle substituent. Figures 8 and 9 reveal that PTNPY shows three absorption bands in the visible range: two are due to the non-participant electrons of the carbanion. The ylid TTNPY possesses two visible bands (Figure 9). Figures 5b and 7b show that the visible bands of both p-nitro-phenacylid-1,2,4-triazol-1-ium ylids are due to electronic transitions from the ylid carbanion towards the p-nitro-phenacyl substituent.
Both the presence of the methyl group in para position of the phenyl substituent at heterocycle and the nitro group substituted to the ylid carbanion determine the difference between the mechanisms of the electron cloud restructuration in the visible absorption process by PTNPY and TTNPY compared with PTPY and TTPY.

So, by using the quantum mechanical computations, the mechanism of the charge transfer induced by the visible photons’ absorption has been explained and the sense of the electronic charge shift becomes evident from the symmetry of the LUMO and HOMO of the studied ylids.

The visible bands of PTPY and TTPY are due to the electron absorption transition between HOMO and LUMO (see Figures 8 and 9). In the case of the isolated molecule (in its gaseous state), the electron density passes from the carbanion towards the heterocycle (this fact is certified by Figures 4b and 6b), while in hydroxyl solvents, the electrons are dispersed on the entire molecule (Figures 4d and 6d). The visible bands of PTPY and TTPY shift to blue when the spectrally active molecules pass from the gaseous phase in hydroxyl solutions, resulting from the quantum mechanical computations. This fact and its disappearance in acid media, experimentally evidenced, certify the attribution of this band to an $n-\pi^*$ transition with electron charge transfer.

In the case of PTNPY and TTNPY, the visible absorption induces an increase in the electron density on the nitro-phenacyl substituent (Figures 5b and 7b), both in a vacuum state and in hydroxyl solutions. The visible bands of PTNPY and TTNPY are shifted to red in hydroxyl solvents compared to the gaseous phase (Figures 8 and 9 and Table 6). This fact proves that the visible bands of the ylids containing a nitro group in phenacyl substituent

**Figure 8.** Energy levels of PTPY and PTNPY in vacuum, water and ethanol computed by Spartan’14.
appear by transitions $\pi-\pi^*$ in which an increase of the electronic charges on the carbanion substituent was computed (see Figures 5 and 7).

Figure 9. Energy levels of TTPY and TTNPY in vacuum, water and ethanol computed by Spartan’14.

Table 6. Computed and experimental wavenumbers for the visible electronic absorption bands of the studied triazolium ylids.

|                | PTPY    | TTPY    | PTNPY   | TTNPY   |
|----------------|---------|---------|---------|---------|
| Experimental [14,15] |         |         |         |         |
| Water          | 25,970  | 27,030  | 27,120  | 28,110  |
| Ethanol        | 25,620  | 26,670  | 26,720  | 27,690  |
| Theoretical (computed with Spartan’14) |         |         |         |         |
| Water          | 29,280  | 29,360  | 28,393  | 28,070  |
| Ethanol        | 29,118  | 29,199  | 28,312  | 28,393  |
| Vacuum         | 28,392  | 25,247  | 29,844  | 30,779  |
| Free term in (1) $\nu_0$ (cm$^{-1}$) | 24,680  | 25,949  | 25,381  | 24,915  |

3.2. Spectral Results

The visible electronic absorption spectra of the studied ylids are given in Figure 10. Small quantities of acetic acid were added in binary solutions of ylids in order to verify whether nonparticipant electrons are implied in the charge transfer caused by visible
photons’ absorption. The disappearance of some bands in acid media proves the charge transfer of the nonparticipant electrons. The sense of the intramolecular charge transfer depends on the structural features of the heterocycle and of the carbanion substituent, as the quantum mechanical analysis emphasized.

Figure 10. Visible electronic spectra of the studied ylids. (a) PTPY and TTPY; (b) PTNPY and TTNPY.

The experimental values of the wavenumbers measured in water and in ethanol for the studied ylids are written in Table 6. The computed values for isolated molecules and for their solutions in water and ethanol (from Table 6) were obtained by HOMO and LUMO expressed in cm$^{-1}$ using the data in eV from Tables 2–5. The values $\nu_0$ (cm$^{-1}$) were obtained by Linear Energy Relationships (LERs) applied to the spectral data (previously published [14,15] for ternary solutions ylid + water + ethanol of the studied ylids) using the solvent parameters measured by Buhvestov and coworkers [16]. The values written in the last row of Table 6 have the significance [14,15] of the wavenumber in the maximum of the visible band of the isolated ylids under the study, as it results from LERs applied to wavenumbers of the studied ylids measured in ternary solutions [14,15]. They are of the same order of magnitude with the values computed for the same transition by Spartan’14.

The probability of the absorption transitions at about 17,000 cm$^{-1}$ (predicted by computation results, see Figures 8 and 9) is very small and consequently they are of
reduced intensity in the electronic spectra of PTNPY and TTNPY solutions (Figure 10b). The bands of PTNPY and TTNPY having the smallest wavenumbers in Figures 8 and 9 appear as shoulders of the smallest intensity (Figure 10) in the electronic absorption spectra. The electronic absorption bands from this spectral range cannot be clearly evidenced in the visible range and were not recorded for this study.

One can see (Table 6) that the experimental and the theoretical wavenumbers of the visible bands are comparable for PTPY and TTPY, while for the ylids PTNPY and TTNPY, the experimentally measured wavenumbers are higher compared with those resulting from the absorption transitions between the energetic levels computed by Spartan’14. The similar values with those experimentally determined for ylids PTNPY and TTNPY are obtained only for absorption bands with wavenumbers written in Table 6.

The wavenumber in the maximum of the visible electronic absorption band of the studied ylids measured in various solvents can be expressed as linear functions on the solvent parameters by empirically established relationships [23,24]. One of these dependences proposed by Kamlet Abboud Taft [24] was used.

\[
\nu = \nu_0 + C_1 \pi^\star + C_2 \alpha + C_3 \beta. \quad (1)
\]

The significance of the parameters in relation (1) is as follows: \(\nu\) is the wavenumber in the maximum of the electronic absorption band measured in a given solvent with parameters \(\pi^\star\) (polarity/polarizability), \(\alpha\) (HBD, or acidity) and \(\beta\) (HBA, or basicity). The correlation coefficients \(\nu_0\) and \(C_1–C_3\) were determined by LERs [25–28] statistical methods. The free term in (1) signifies the wavenumber in the maximum of the electronic absorption band for the isolated solute molecule (in a vacuum state) and \(C_1–C_3\) are proportional with the strength of the intermolecular interactions in solution. The values of \(\nu_0\) for the studied ylids are written in the last row of Table 6. The terms \(C_1 \pi^\star, C_2 \alpha\) and \(C_3 \beta\) give, by their magnitude, the contribution of each type of interaction to the spectral shift in the given solvent and by their sign they show the sense of the spectral shift determined by the respective interaction.

The correlation coefficients obtained for the ternary solutions of the studied 4-aryl-1,2,4-triazol-1-ium methylidins in binary solvents water (1) + ethanol (2) were established using the experimental data from [14,15] and KAT coefficient from [16] (relation (1)). They were used to write the relations (2)–(5).

PTPY:

\[
\nu = (24,680.3 \pm 173.2) + (676.0 \pm 53.6)\pi^\star + (243.3 \pm 47.0)\alpha + (413.2 \pm 119.5)\beta; \quad R = 0.99 \quad (2)
\]

PTNPY:

\[
\nu = (25,381.4 \pm 413.9) + (794.8 \pm 128.1)\pi^\star + (364.6 \pm 112.3)\alpha + (668.1 \pm 285.5)\beta; \quad R = 0.97 \quad (3)
\]

TTPY:

\[
\nu = (25,949.2 \pm 231.2) + (696.0 \pm 71.6)\pi^\star + (108.0 \pm 62.8)\alpha + (291.0 \pm 159.5)\beta; \quad R = 0.99 \quad (4)
\]

TTNPY:

\[
\nu = (24,915.3 \pm 309.9) + (1484.5 \pm 95.9)\pi^\star + (449.9 \pm 84.1)\alpha + (1879.8 \pm 213.8)\beta; \quad R = 0.99 \quad (5)
\]

Relations (2)–(5) contain all terms with positive signs, showing that the visible bands of the studied ylids shift to blue when the solvent KAT parameters increase, due to the increase of the water content in binary solvent. Using relations (2)–(5), the contribution of each type of interaction to the spectral shifts was computed. The dependence of these contributions, expressed in percent, vs. the water molar fraction in the binary solvent, is plotted in Figure 11 for PTPY and PTNPY in binary solvent mixtures of water (1) + ethanol (2).

Similar dependences of the contribution of the intermolecular interactions to the spectral shifts recorded in ternary hydroxyl solutions of TTPY and TTNPY were also obtained [15], both in water + ethanol and in water + methanol.
The contribution of each type of interaction to the spectral shifts recorded in electronic absorption spectra can be evaluated for the ternary solutions of the studied ylids by applying the LERs for the dependence of type (1) between the wavenumbers of the visible band of ylids and KAT solvent parameters.

Figure 11 shows that, for PTPY, the highest spectral shift is due to the universal (orientation, induction and dispersion) interactions described by the term $C_1 \pi^*$, which increases with the water–molar fraction in the binary hydroxyl solvent.

The term $C_2 \alpha$ from relation (1) gives the contribution to the spectral shift of the specific interactions in which hydrogen bonds are realized with the exception of protons by ylid molecules. Due to the basic nature of the studied ylids and the hydroxyl character of the two liquids from binary solvent mixtures, in all studied solutions there are complexes of the types: ylid–water and/or ylid–ethanol. The two types of complexes coexist in the ternary solutions, their relative numbers being dependent on the water content of the binary solvent. The probability of free ylid molecules existing in the studied solutions is much reduced. Consequently, the contribution of the term $C_2 \alpha$ to the total spectral shift of the visible band is the smallest for all studied ylids in binary solvent mixtures (BSMs).

The contribution to the spectral shift of the term $C_3 \beta$ is smaller than 45% and decreases with water content in the binary solvent for both PTPY and TTPY methylids. The presence of the interactions in which the ylids donate protons to hydroxyl solvent could be explained by the fact that hydrogen bonds in the complexes ylid–water and ylid–ethanol are very weak and at room temperature, in which the experiments were conducted, they can be destroyed by thermal motion, determining the existence of free protons in solutions.

The term $C_2 \alpha$ also makes the smallest contribution to the spectral shifts of the visible band for PTNPY and TTNPY; even the hydrogen bonds between ylids and hydroxyl groups of the solvents are more probable than in the cases of PTPY or TTPY.

For small water concentrations in binary solvent, $x_1 < 0.3$ in the case of PTNPY and $x_1 < 0.8$ for TTNPY, the highest contribution to the total shifts of the visible band is due to the specific interactions in which the solvent molecules receive protons, described by the term $C_3 \beta$. For $x_1 > 0.3$ in the case of PTNPY and $x_1 > 0.8$ in the case of TTNPY, the contribution of the universal interactions of the type orientation–induction becomes prevalent. The term $C_1 \pi^*$ increases with the water–molar fraction in the binary solvent, as shown in Figure 11. Concomitantly, the term $C_3 \beta$ decreases with the increase in $x_1$.

The dependences illustrated in Figure 11 show that the orientation–induction interactions are strengthened based on the increase of the water content in binary solvent, while the specific interactions described by the term $C_3 \beta$ decrease.

Table 7 contains the contribution of the universal interactions (described by $\pi^*$), and specific interactions in which the ylid molecule receives protons (described by $\alpha$) and
donates protons (described by $\beta$) in water and in ethanol, as they can be evaluated by using the LERs correlation coefficients from relations (2)–(5) and the solvent parameters for these solvents listed in [16].

**Table 7.** Contribution of the intermolecular interactions (in percent) in water and ethanol solutions of the studied ylids.

| Solvent | Ylid  | $C_1\pi^*$ (%) | $C_2\alpha$ (%) | $C_3\beta$ (%) |
|---------|-------|----------------|-----------------|----------------|
| Water   | PTPY  | 60             | 24              | 16             |
|         | PTNPY | 53             | 27              | 20             |
|         | TTPY  | 74             | 13              | 13             |
|         | TTNPY | 53             | 18              | 29             |
| Ethanol | PTPY  | 37             | 26              | 37             |
|         | PTNPY | 31             | 27              | 42             |
|         | TTPY  | 51             | 15              | 34             |
|         | TTNPY | 27             | 16              | 57             |

The data from Table 7 show the great contribution of the universal interactions for the studied ylids.

In the water solutions of all the studied ylids, the contribution of the universal interactions is higher than 53%, while the specific interactions, described by the terms $C_2\alpha$ and $C_3\beta$, have contributions between 13% and 29%.

In the ethanol solutions of the studied ylids, the universal interactions are weaker than in the water solutions, but still in the range 27–51%. Among the specific interactions, those described by the term $C_3\beta$ are dominant, their contribution being in the range 34–57%.

As remarked in [16,29,30], water molecules can form cages around the solute molecule or its complex, isolating them from the alcohols’ molecules.

The ylids PTNPY and TTNPY are characterized by six HBD counts, while PTPY and TTPY have only three HBA counts.

The computed data with relations (2)–(5) are in a good agreement with the experimental data measured for the ternary solutions ylid + water + ethanol, as shown in Figure 12.

![Figure 12](image.png)

**Figure 12.** Calculated wavenumbers vs. experimental wavenumbers for the solution ylid + water + ethanol of (a) PTPY and (b) PTNPY (experimental data from [14]).

In Figure 12, the dependence between the wavenumbers computed based on relation (1) and those determined experimentally is illustrated for two studied ylids using relations (2)–(5). A good concordance is illustrated in Figure 12 for PTPY and PTNPY.
The spectral data referring to the visible bands of the studied p-aryl-1,2,4-triazol-1-i um phenacylids recorded in mixtures of water +ethanol were analyzed by LERs using quasi-empirical linear multi-parameters relation (6):

$$
\nu \left( \text{cm}^{-1} \right) = \nu_0 + C_1 f(\epsilon) + C_2 f(n) + C_3 \alpha + C_4 \beta,
$$

for which the correlation parameters $C_1$ and $C_2$ have theoretical signification [25–28], as results from the theories of McRae [31] or Bakhshiev [32]. In relation (6), $f(\epsilon) = \frac{\epsilon^2 - 1}{\epsilon^2 + 2}$ and $f(n) = n^2 - 1$ are the polarity and polarizability functions [23,31] of a given solvent depending on the electric permittivity, $\epsilon$, and refractive index, $n$. The polarity/polarizability solvent parameters, $\pi^*$, linearly depend on the solvent functions, $f(\epsilon)$ and $f(n)$ [23]. Having in view the theoretical significance of the coefficients $C_1$ and $C_2$ from relation (6), expressed by relations (7) and (8), one can estimate the value of the excited state dipole moment of molecules if its value in the ground state is known. Based on quantum mechanical calculations, one can also establish the angle between the molecular dipole moments in the electronic state responsible for the visible band appearance.

$$
C_1 = \frac{2 \mu_g (\mu_g - \mu_e \cos \varphi)}{h c r^3} + 3 k T \frac{\alpha_g - \alpha_e}{r^3},
$$

$$
C_2 = \frac{\mu_g^2 - \mu_e^2}{h c r^3} - C_1 + \frac{3}{2} \frac{\alpha_g - \alpha_e}{I_u + I_v} I_u I_v.
$$

In relations (7) and (8), $\mu$ is the dipole moment; $\alpha$ is the electric polarizability; $I$ signifies the ionization potential of the solute (index $u$) and solvent (index $v$), $T$ is the absolute temperature, $h$ is the Planck’s constant, $c$ is light velocity and $r$ is the molecule’s radius. The indices $g$ and $e$ refer to the ground and excited electronic states, respectively.

The correlation coefficients obtained for relation (6) with the data from Table 8 are written in Table 9.

**Table 8.** Binary solvent mixture parameters for water (1) + ethanol (2) and wavenumbers in the maximum of the visible band of the studied ylids.

| $x_1$ | $f(\epsilon)$ | $f(n)$ | $\alpha$ | $\beta$ | $\nu$ (cm$^{-1}$) |
|-------|---------------|--------|----------|-------|----------------|
| 0.0   | 0.886         | 0.205  | 0.83     | 0.98  | 25,620 26,720 26,670 27,690 |
| 0.05  | 0.886         | 0.206  | 0.83     | 0.97  | 25,625 26,730 26,680 27,720 |
| 0.10  | 0.889         | 0.207  | 0.84     | 0.96  | 25,640 26,740 26,690 27,748 |
| 0.15  | 0.895         | 0.208  | 0.83     | 0.94  | 25,652 26,750 26,700 27,778 |
| 0.20  | 0.899         | 0.209  | 0.83     | 0.93  | 25,665 26,760 26,718 27,810 |
| 0.25  | 0.901         | 0.210  | 0.83     | 0.93  | 25,680 26,770 26,730 27,840 |
| 0.30  | 0.904         | 0.210  | 0.82     | 0.92  | 25,696 26,785 26,748 27,868 |
| 0.35  | 0.909         | 0.211  | 0.81     | 0.91  | 25,710 26,800 26,760 27,896 |
| 0.40  | 0.912         | 0.212  | 0.80     | 0.91  | 25,720 26,815 26,780 27,920 |
| 0.45  | 0.917         | 0.213  | 0.79     | 0.89  | 25,738 26,834 26,800 27,940 |
| 0.50  | 0.921         | 0.214  | 0.79     | 0.90  | 25,752 26,850 26,818 27,958 |
| 0.55  | 0.925         | 0.215  | 0.78     | 0.89  | 25,760 26,870 26,830 27,980 |
| 0.60  | 0.930         | 0.215  | 0.77     | 0.89  | 25,778 26,890 26,850 28,000 |
| 0.65  | 0.934         | 0.216  | 0.77     | 0.89  | 25,792 26,910 26,877 28,020 |
| 0.70  | 0.939         | 0.217  | 0.74     | 0.88  | 25,815 26,924 26,898 28,038 |
| 0.75  | 0.944         | 0.217  | 0.71     | 0.86  | 25,830 26,940 26,920 28,040 |
| 0.80  | 0.948         | 0.218  | 0.67     | 0.87  | 25,850 26,960 26,940 28,066 |
| 0.825 | 0.950         | 0.219  | 0.66     | 0.87  | 25,865 26,970 26,950 28,070 |
| 0.850 | 0.952         | 0.219  | 0.64     | 0.90  | 25,874 26,978 26,964 28,080 |
| 0.875 | 0.955         | 0.219  | 0.61     | 0.92  | 25,888 26,980 26,978 28,088 |
| 0.90  | 0.956         | 0.220  | 0.59     | 0.97  | 25,900 26,990 26,988 28,090 |
Table 8. Cont.

| $x_1$ | $f(\epsilon)$ | $f(n)$ | $\alpha$ | $\beta$ | $\bar{v}$ (cm$^{-1}$) |
|-------|----------------|--------|----------|--------|----------------------|
| 0.925 | 0.957          | 0.220  | 0.56     | 1.03   | PTPY 25,915          |
| 0.950 | 0.999          | 0.221  | 0.54     | 1.11   | PTPY 25,926          |
| 0.975 | 0.962          | 0.221  | 0.52     | 1.18   | PTPY 25,948          |
| 1.00  | 0.963          | 0.222  | 0.50     | 1.26   | PTPY 25,970          |
|       |                |        |          |        | PTNPY 27,000         |
|       |                |        |          |        | PTNPY 27,020         |
|       |                |        |          |        | PTNPY 27,040         |
|       |                |        |          |        | PTNPY 27,120         |
|       |                |        |          |        | TTPY 27,008          |
|       |                |        |          |        | TTPY 27,012          |
|       |                |        |          |        | TTPY 27,030          |
|       |                |        |          |        | TTNPY 28,095         |
|       |                |        |          |        | TTNPY 28,102         |
|       |                |        |          |        | TTNPY 28,105         |
|       |                |        |          |        | TTNPY 28,110         |

Table 9. Correlation coefficients in relation (6) for the studied ylids in water (1) and ethanol (2) solvent mixtures and regression coefficient, R.

| Ylid   | $\nu_0 \pm \Delta \nu_0$ | $C_1 \pm \Delta C_1$ | $C_2 \pm \Delta C_2$ | $C_3 \pm \Delta C_3$ | $C_4 \pm \Delta C_4$ | R   |
|--------|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----|
| PTPY   | 22,401 ± 147             | 1008 ± 768            | 11,703 ± 3407         | 182 ± 44              | 72 ± 19               | 0.999 |
| PTNPY  | 22,110 ± 494             | 6545 ± 2572           | -8227 ± 1143          | 279 ± 148             | 283 ± 65              | 0.989 |
| TTPY   | 23,390 ± 165             | 3485 ± 862            | 1797 ± 387            | -191 ± 50             | -18 ± 22              | 0.999 |
| TTNPY  | 19,016 ± 4157            | 17,879 ± 2166         | -39,805 ± 9612        | 1205 ± 1245           | 52 ± 55               | 0.677 |

This study was conducted in order to use the values of the correlation coefficients $C_1$ and $C_2$ for estimating the excited state electric dipole moment of the studied ylids and for approximating the angle between the dipole moments in the electronic states responsible for the absorption process of the visible photons. The procedure described in [30,33] was applied for these calculations.

The results obtained for estimating the excited dipole moment of the studied ylids for the visible absorption transitions using relations (7) and (8), the molecular parameters from Tables 2–5 and the procedure described in [30,33], are given in Table 10.

Table 10. Dipole moments and polarizability in the electronic states responsible for the visible absorption band and the angle between dipole moments for the studied triazolium ylids.

| Ylid   | $\mu_g$ (D) | $\mu_e$ (D) | $\varphi$ (degree) |
|--------|--------------|--------------|---------------------|
| PTPY   | 10.61        | 22.51        | 61.33               |
| PTNPY  | 18.66        | 18.40        | 18.00               |
| TTPY   | 11.22        | 23.50        | 62.43               |
| TTNPY  | 19.19        | 21.57        | 37.45               |

The values of the excited state dipole moments were obtained, hypothesizing that the excited state polarizability must be a positive parameter as it results from its definition for the case of PTPY and TTPY and in the hypothesis of McRae [31] and Kawski [34] (in the time of electronic transition the molecular polarizability is the same in the electronic state participating to the absorption transition) for ylids PTNPY and TTNPY. The angle between the excited and the ground states of the electronic transition is smaller in the case of PTNPY and TTNPY compared with those for PTPY and TTPY. By comparing the HOMO and LUMO maps of the studied ylids in Figures 4–7, one can say that in the case PTNPY and TTNPY the absorption transition produces the shift of the valence electron cloud towards the carbanion, while in the case of PTPY and TTPY it is dispersed on the entire molecule.

The spectral data obtained for ternary solutions ylid + water (1) + ethanol (2), in which the index (1) shows the more active solvent from the interaction’s point of view, can be interpreted based on the results obtained from the statistical model of ternary solutions [35–38] in which a dependence of the type

$$\ln \frac{p_1}{1-p_1} = \ln \frac{x_1}{1-x_1} + \frac{w_2-w_1}{kT}$$

(9)
is established between the statistical average weight, \( p_1 \), of the active solvent in the first solvation shell of the solute and the molar fraction of the same solvent in the bulk solution, \( x_1 \). In Equation (9), the interaction energies in molecular pairs of the types ylid–water and ylid–ethanol are noted by \( w_1 \) and \( w_2 \), respectively. The average statistical weight of water in the first solvation shell of a ylid molecule can be computed using the wavenumbers in the maximum of the visible band of the ylid measured in the ternary solution (\( \nu_1 \)) and in the two solvents water (\( \nu_2 \)) and ethanol (\( \nu_3 \)), by using the formula:

\[
p_1 = \frac{\nu_1 - \nu_2}{\nu_1 - \nu_3}.
\]  

(10)

The dependences of the type (9) for the studied ylids are illustrated in Figure 13.

![Figure 13.](image)

**Figure 13.** \( \ln \frac{p_1}{1-p_1} \) vs. \( \ln \frac{x_1}{1-x_1} \) for ternary solution ylid + water + ethanol of (a) PTPY and (b) PTNPY.

Similar dependences were obtained in the case of TTPY and TTNPY ternary solutions in water + ethanol [15].

Based on the results from Figure 13, the difference \( w_2 - w_1 \) can be computed [37,38] (see Table 11). For PTPY, TTPY and PTNPY this difference is negative, indicating that \( |w_2| > |w_1| \), that is, the hydrogen bond ylid–ethanol is stronger than the hydrogen bond ylid–water, while for TTNPY this difference is positive, signifying the stronger hydrogen bond of the ylid with water, compared with ethanol molecules.

**Table 11.** Difference \( w_2 - w_1 \) for the studied ternary solutions in binary solvent water + ethanol.

| Ylid  | \( x_1 \) | \((w_2 - w_1) \times 10^{20} \text{ (J)}\) |
|-------|--------|---------------------------------|
| PTPY  | <0.5   | -0.139                          |
|       | >0.5   | -0.229                          |
|       | <0.7   | -0.306                          |
| PTNPY | >0.7   | -0.090                          |
| TTPY  |        | -0.163                          |
| TTNPY |        | 0.247                           |

The obtained differences \( w_2 - w_1 \) from Table 11 are very small due to the fact that hydrogen bonds realized by receiving protons take place in both hydroxylic solvents, and also both liquids have polar molecules which determine the orientation interactions of comparable strength.

For the ylids PTPY and PTNPY, this difference changes its value at a given value of the water molar fraction in the binary solvent (Table 11), demonstrating that at small water concentrations in the ternary solutions, the complexes of the type ylid–ethanol are predominant, while for high water content in binary solvent, the complexes of the type ylid–water are predominant.
In the case of tolyl-1,2,4-triazolium methylids, the difference \( w_2 - w_1 \) has a single value for all water molar concentrations in binary solvent, as shown in Table 11. The types of complexes formed in ternary solutions do not influence this dependence.

The computed statistical weight of water molecules in the first solvation shell of the spectrally active molecules is higher than the molar fraction of water in the bulk binary solvent, influencing the ability of the molecules from the first solvation cell of solute to orient the ylid–water complex. At small water molar concentrations in binary solvent, the number of complexes of the type ylid–alcohol is higher than the number of the complexes of ylid–water. The situation is changed at high water concentrations. This is one of the causes of changing the slopes of the dependences (9) for PTPY and for PTNPY.

A second cause can be the changes in water structure at its high concentrations in a binary solvent [29,30]. The results obtained in this paper demonstrate the ability of water molecules to interact by way of hydrogen bonds, by forming cages around the hydrophobic parts of solute molecules, especially at high binary solvent content in water [16,29].

4. Conclusions

Four carbanion monosubstituted p-aryl-1,2,4-triazol-1-ium methylids were studied from a computational point of view in comparison with previous results obtained by spectral studies of the same molecules in the hydroxyl binary solvent water + ethanol.

Quantum mechanical representations obtained by the Spartan 14 program were used in order to explain the nature of the electronic transitions responsible for the visible absorption band and to establish the sense of the electrons’ shift in the intramolecular charge transfer caused by the visible photons’ absorption.

A good agreement was obtained between the wavenumber computed by LERs applied to ternary solutions and that computed by Spartan’14 values corresponding to the isolated ylid molecules and for the same molecules in solutions with water and ethanol.

By plotting the energy levels computed by Spartan’14 programs, the possible electronic transitions in absorption for the visible range of the four ylids were obtained and then compared with those experimentally measured. The sense of the electron transition for the visible band appearance in the case of 4-aryl-1,2,4-triazol-1-ium-4-nitro-phenacylides differs from that produced in the 1,2,4-triazol-1-ium ylids, having a carbanion substituent phenacyl group.

The computations show that there is an \( n-\pi^* \) transition at lower wavenumbers in the case of PTNPY and TTNPY corresponding to an electronic band of very low intensity. Some specifications regarding the direction in which the charge transfer takes place were made by comparing the HOMO and LUMO representations of the studied molecules in a vacuum and in hydroxyl solvents.

The computed values of the water statistical weight (considered as being more active from the interaction point of view compared with ethanol molecules) in the first shell of the ylid molecules are higher than the water molar concentration in the bulk solution.

The difference \( w_2 - w_1 \) is negative for the ternary solutions in water + ethanol for PTPY, TTPY and PTNPY, but it is positive in the case of the ylid TTNPY. This fact demonstrates that, for the TTNPY molecule, the specific interaction with ethanol molecules is smaller than with water molecules. For all other ylids, PTPY, TTPY and PTNPY, the specific interactions between the ethanol and the ylid molecules are stronger compared with those between the ylids with water molecules, as shown by the inequality \( \|w_2\| > \|w_1\| \).

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