

Article

Computational and Spectral Means for Characterizing the Intermolecular Interactions in Solutions and for Estimating Excited State Dipole Moment of Solute

Dana Ortansa Dorohoi ^{1,*}, Dorina Emilia Creanga ¹, Dan Gheorghe Dimitriu ¹ , Ana Cezarina Morosanu ¹, Antonina Gritco-Todirascu ¹, Gabriel Grigore Mariciuc ², Nicoleta Puica Melniciuc ³, Elena Ardelean ³ and Corina Cheptea ⁴

¹ Faculty of Physics, Alexandru Ioan Cuza University, 11 Carol I Blvd., RO-700506 Iasi, Romania; mdor@uaic.ro (D.E.C.); dimitriu@uaic.ro (D.G.D.); cezarina_morosanu@yahoo.com (A.C.M.); antoninagritco@yahoo.com (A.G.-T.)

² Faculty of General Medicine, Gr. T. Popa University of Medicine and Pharmacy, 16 Universității Street, RO-700115 Iasi, Romania; gabrielgrigoremariuc@students.umfiasi.ro

³ Faculty of Orthodox Theology, Alexandru Ioan Cuza University, 6 Closca Street, RO-700066 Iasi, Romania; nicoleta.melniciuc@uaic.ro (N.P.-M.); elena.ardelean@uaic.ro (E.A.)

⁴ Faculty of Biomedical Sciences, Gr. T. Popa University of Medicine and Pharmacy, 9-13 M. Kogalniceanu Street, RO-700454 Iasi, Romania; corina.cheptea@umfiasi.ro

* Correspondence: ddorohoi@uaic.ro

Received: 8 July 2020; Accepted: 29 July 2020; Published: 4 August 2020



Abstract: The results obtained both in quantum chemical computation and in solvatochromic study of pyridinium di-carbethoxy methylid (PCCM) are correlated in order to estimate the electric dipole moment in the excited state of this molecule. This estimation is made by a variational method in the hypothesis that the molecular polarizability does not change in time of the absorption process. Ternary solutions of PCCM in protic binary solvents are used here, both establishing the contribution of each type of interaction to the spectral shift and to characterize the composition of the first solvation shell of PCCM. Results are compared with those obtained before for other binary solvents. The difference between the interaction energies in molecular pairs of PCCM-active solvent and PCCM-less active solvent was also estimated based on the cell statistical model of the ternary solutions.

Keywords: pyridinium di-carbethoxy methylid; visible intramolecular charge transfer absorption band; excited state dipole moment; intermolecular interactions in binary and ternary solutions; energy in the molecular pairs

1. Introduction

Knowledge about the electro-optical parameters of molecules in different electronic states obtained by experimental means is of the greatest importance for the researchers working in quantum chemistry field, either for comparison with theoretical data or for overtaking some steps of calculations based on them.

The electronic spectra (absorption or fluorescence) involve the valence electronic cloud very sensitive to the external fields. In solutions, the solute (spectrally active) molecules are under the action of the internal electrostatic field created by the solvent molecules surrounding them (named by Onsager internal reactive field [1]). The strength of the interactions between the solute and a given solvent depends both on the internal reactive field magnitude and on the electro-optical parameters of the spectrally active molecule.

The molecular parameters are usually different in the two electronic states between which the absorption transition takes place. Consequently, the difference of the solvation energies of the solute (in the electronic states responsible for the electronic band appearance) determines the spectral shift [2–4] in solvent related to the vacuum state (vaporous state of the solute).

Information on the intermolecular interactions strength in liquids can be obtained from the spectral shifts of the electronic bands. Thus, the spectrally active molecules can be used as probes in testing the internal field in different liquids.

Based on the existent theories regarding the solvent influence on the electronic bands, one can establish the nature and the strength of the intermolecular interactions in different liquids, or one can estimate some electro-optic parameters in the electronic states of the spectrally active molecules [5–10] (in the limits in which these theories were developed). This kind of information is useful both for quantum mechanics and for developing the liquid theory, which, in the actual stage, cannot generalize in mathematical treatment all phenomena occurring in this state of matter. The insurmountable difficulty for the liquid theories is the gentle equilibrium between the strength of the internal interactions and the thermal motion energy which generates a continuous order–disorder in the molecular arrangement. For these reasons, the study of the electronic spectra in liquids with various physicochemical properties offers more information about the molecular structure of liquids, compared with FTIR or Raman spectra, which emphasize only the local modification in the structural features of the studied molecules.

Pyridinium di-carbethoxy methylid (PCCM) was chosen as the spectrally active molecule in this study.

Pyridinium ylids are zwitterionic compounds in which the positively charged heterocycle (pyridine) is covalently bonded to a negative carbanion bearing a positive charge [11]. Pyridinium ylids [11–13] are important in chemistry, especially because they are precursors in obtaining new organic compounds. Pyridinium ylids are suitable building blocks [14] from the synthesis of indolizines, cyclopropanes, 2(1H)-pyridin-(ethio)-ones, cyclopropanes, 2,3-dihydrofuranes, mono-oligopyridines, pyranonaphthoquinones, nitrones, or azepines. Pyridinium ylids are nucleophilic molecules with long lifetime used in 1,3 dipolar cycloaddition chemistry [15–17]. In cycloaddition of pyridinium ylids with alkene made in aqueous buffer at room temperature [17], the highest yield was obtained for electron withdrawing groups attached both to ylids and alkenes.

The carbanion centers of the ylid-partial structures can serve as electron donators in the reversible color changes [18] for the photochromatic Merrifield resins.

Pyridinium ylids are used in some applications based on polymers [19–21]. The UV exposure of pyridinium ylid accompanied by a change in polarity was applied in photo resistors. Polymers containing pyridinium ylids were prepared [19] as water soluble MID UV resist materials. Pyridinium ylids and their salts are used to obtain photochromic materials, such as photosensitive resins [20], due to their reversible color change in which the carbanion lone electron pair is implied. Some novel negative photoresists were obtained [20] based on the photo isomerization of water- soluble polymeric pyridinium ylid.

Polymers containing pyridinium ylid moieties were subjected to actinic irradiation in order to convert the pyridinium ylid moieties to water-insoluble N-acyl diazepine polymers [21], used for the water-proofing or hydrophobization of surfaces, as well as for the production of photoresists, printing plates, and printed circuit boards.

In material science, pyridinium ylids were also used for obtaining thin conducting layers [22,23].

As all cycloimmonium ylids [14–17], pyridinium ylids show a visible electronic absorption band due to an intramolecular charge transfer from the carbanion toward the heterocycle. This band is very sensitive to the solvent nature. Due to this spectral property, pyridinium ylids can be used as acid–basic indicators [11,24].

Pyridinium ylids were used in physics as probes to characterize the strengths of the internal electric field in solutions [11,24].

Both the quantum mechanical and solvatochromic studies can give interesting details regarding the structural features in the electronic state responsible for the pyridinium ylid visible band appearance [24–28].

Pyridinium di-carbethoxy methylid (PCCM) [11] is an amphiphilic compound with the positive charge located on the nitrogen atom belonging to pyridine heterocycle and the negative charge distributed on the carbanion double substituted by the carbethoxy groups (Figure 1). The symmetrically substituted carbanion increases the stability of PCCM [29–31].

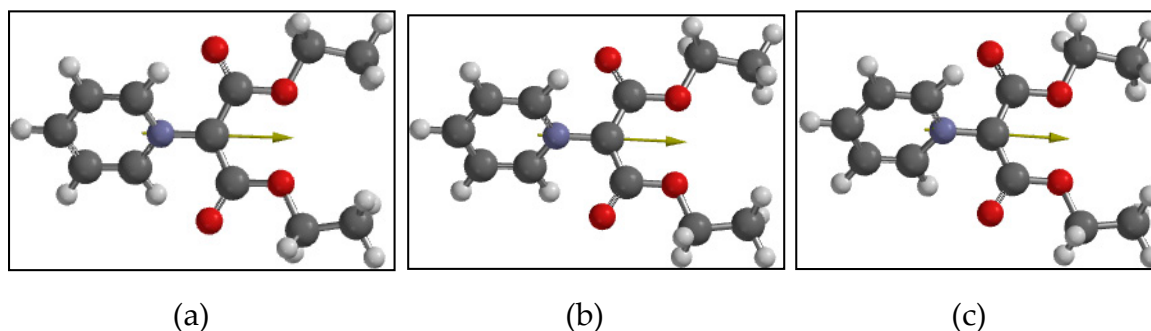


Figure 1. Optimized structures of pyridinium di-carbethoxy methylid (PCCM) in (a) vacuum, (b) water, and (c) ethanol.

The aim of this study was to use the spectral data obtained for PCCM binary and ternary solutions in order to obtain information about the excited state dipole moment of ylid and the nature and the strength of the intermolecular interactions in diluted ylid solutions. The difference between the potential energies in molecular pairs achieved between the ylid and the hydroxyl solvent molecules in ternary solutions is also estimated in this study.

The inhomogeneity of the first solvation shell of ylid in ternary solutions was also evidenced, by estimating the molar fractions of the two solvents in the first solvation shell of PCCM. The results can be compared with those obtained for a pyridinium ylid with non-symmetrical carbanion, pyridinium acetyl benzoyl methylid (PABM), or for benzo-[f]-quinolinium acetyl benzoyl methylid (BQABM) published before [28,32].

2. Experimental and Computational Details

The studied substance was prepared as it is described in Reference [11], in the Alexandru Ioan Cuza University labs. The purity of the obtained substance was checked by spectral (NMR and IR) and chemical (elemental) means.

The spectrally grade solvents were achieved from Merck Company and Fluke (Sigma-Aldrich) and used without any purification.

The solvent parameters were taken from <https://www.stenutz.eu/chem.solv26.php>.

The binary solvents used in this study were achieved in molar fractions from double-distilled water, ethanol, and methanol.

The visible electronic absorption band was recorded at a Specord UV-Vis Carl Zeiss Jena spectrophotometer.

The quantum mechanical analysis was made by Spartan'14 program, using EDF2/6–31G* density functional model [33].

Statistical analysis was made by using Origin 9.

3. Theoretical Notions

The optimized geometry (the arrangement of molecular atoms for which the molecular energy is minim) and some energetic, electro-optical, and QSAR parameters of the PCCM molecule in electronic ground state were established in computational estimations with Spartan'14 program.

Some of the data obtained in quantum mechanical analysis are used here for estimating, in a variational method, the excited state dipole moment of PCCM based on solvatochromic results. In this method, a relation is established between the excited dipole moment and the polarizability of PCCM, and then the excited state dipole moment is determined in the McRae [2] and Kawschi [7,34] hypothesis that the molecular polarizability does not change during of electronic transition responsible for the visible band appearance.

The solvent influence on the visible band of PCCM was explained both by using empirical parameters introduced by Kamlet Taft [35] and also by using Relation (2), derived by the theory of diluted solutions developed by McRae [2], Bakhshiev [3], Abe [4], and others, in the hypothesis that only long-range (universal or non-specific) interactions determine the spectral shifts. In this case, the influence of the specific interactions is taken into consideration by two empirically introduced terms in Relations (1) and (2).

$$\bar{\nu}(\text{cm}^{-1}) = C_1 + C_2\pi^* + C_3\alpha + C_4\beta, \quad (1)$$

$$\bar{\nu}(\text{cm}^{-1}) = \nu_0 + C_1f(\epsilon) + C_2f(n) + C_3\alpha + C_4\beta, \quad (2)$$

with

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2} \text{ and } f(n) = \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

The significance of the parameters in (1)–(3) is the following: $\bar{\nu}(\text{cm}^{-1})$ is the wavenumber in the maximum of the intramolecular charge transfer (ICT) band of PCCM; ϵ and n are the solvent electric permittivity and refractive index; π^* is the solvent polarity/polarizability indicator; and α (HBD) and β (HBA) are the solvent abilities to donate or to accept protons in hydrogen bonds [27,36]. The empirically introduced solvent parameters [35] π^* , α , and β are named Kamlet Taft parameters and are usually used in solvatochromic studies [37,38].

The correlation coefficients, C_1 and C_2 , from Relation (2) depend, as indicated by Relations (4) and (5), on molecular dipole moments, μ ; polarizability, α ; ionization potentials, I ; and temperature, T , at which the experiments are made. The indices g and e refer to ground and excited electronic states, and u and v refer to the solute and solvent molecules, respectively.

$$C_1 = \frac{2\mu_g(\mu_g - \mu_e \cos \varphi)}{hca^3} + 3kT \frac{\alpha_g - \alpha_e}{a^3}, \quad (4)$$

$$C_2 = \frac{\mu_g^2 - \mu_e^2}{hca^3} - \frac{2\mu_g(\mu_g - \mu_e \cos \varphi)}{hca^3} - 3kT \frac{\alpha_g - \alpha_e}{a^3} + \frac{3}{2} \frac{\alpha_g - \alpha_e}{a^3} \frac{I_u I_v}{I_u + I_v}. \quad (5)$$

In (4) and (5), a is the molecular radius, approximated (in the hypothesis that the molecule is a spherical entity) by using Relation (6), and φ is the angle between the dipole moments.

$$a = \frac{3V}{A} \quad (6)$$

The volume, V , and the area, A , from (6) were obtained here by quantum mechanical computations (see Table 1).

The correlation coefficients, C_1 and C_2 , resulting from the solvatochromic analysis, can be used for estimating both the excited state dipole moment and the angle between the electric dipole moments in the electronic state responsible for the electronic band appearance when some electro-optical parameters of the studied molecule are obtained by other methods (for example, by computational methods).

The results obtained in solvatochromic study and the molecular parameters for the PCCM ground electronic state established by Spartan'14 are used here to estimate the dipole moment in the excited state of this molecule.

Table 1. Computed (by Spartan'14) parameters of PCCM for isolated molecule, in water and ethanol solutions.

Molecule Properties			
	Density Functional EDF2, 6–31 G*, in Vacuum	Density Functional EDF2, 6–31 G*, in Water	Density Functional EDF2, 6–31 G*, in Ethanol
Formula	C ₁₂ H ₁₅ NO ₄	C ₁₂ H ₁₅ NO ₄	C ₁₂ H ₁₅ NO ₄
Weight	237.255 amu	237.255 amu	237.255 amu
Energy	−821.401842 au	−821.422833 au	−821.428045 au
Energy (aq)	−821.414893 au	-	-
Solvation E	−34.27 kJ/mol	-	-
E _{HOMO}	−5.12 eV	−5.58 eV	−5.47 eV
E _{LUMO}	−1.93 eV	−1.86 eV	−1.83 eV
Dipole Moment	2.87 Debye	6.28 Debye	6.15 Debye
Tautomers	0	0	0
Conformers	36	36	36
QSAR (Quantitative Structure–Activity Relationship)			
Area	270.44 Å ²	274.40 Å ²	274.30 Å ²
Volume	243.96 Å ³	245.24 Å ³	245.15 Å ³
PSA	35.050 Å ²	37.812 Å ²	37.737 Å ²
Ovality	1.43	1.45	1.45
Polarizability	60.41 Å ³	60.39 Å ³	60.40 Å ³
HBD Count	0	0	0
HBA Count	3	3	3

For the molecules showing electronic spectra both in absorption and fluorescence [3,8,34,39], the correlation coefficients, C_1 and C_2 , are usually transformed in an equations system by introducing molecular parameters of the ground electronic state obtained by quantum mechanical analysis. The excited state dipole moment, the excited state polarizability, and also the angle between the solute dipole moments in the two states of electronic transition are estimated in the limits of approximation in which the theory of liquids was developed [2–5].

There are molecules showing only absorption spectra. In their case, the values of the coefficients, C_1 and C_2 , and the electro-optical parameters theoretically obtained could offer information about the excited state dipole moment by using a variational method [40] applied with good results for other molecules [10,38].

Some relations between the excited state dipole moment, the polarizability, and angle between the dipole moments in the electronic states of the transition are established in this method. Based on these relations, the excited state and polarizability can be computed at each angle (considered as being variable) between the dipole moments. The absorption transition is supposed to be achieved when the excited state polarizability of the solute molecule equalizes the ground state polarizability, in accordance with McRae's [2] or Kawski's [7,34] approximations.

The majority of the publications [40–44] takes into consideration the ground electronic state parameters of the spectrally active molecules computed in quantum mechanics for isolated molecules, in their vaporous state, while in solutions, their parameters can drastically be changed by interactions. This approximation could also influence the value of the excited state dipole moment estimated by using computational and solvatochromic results.

Ternary solutions were used both to enlarge the physical parameters of the liquids used in solvatochromic study and to characterize the local structure of the diluted solutions of PCCM.

Additionally, the statistic cell model of ternary solutions [45–49] applied to PCCM permitted us to estimate the difference between the interaction energies in molecular pairs of the types: ylid-active solvent (1) and ylid-inactive solvent (2). This is a very important result because there are very few methods for estimating the intermolecular energy for molecular pairs in solutions.

The average statistic weight of the most active (from the interactions point of view) solvent in the first solvation shell of the solute molecule, noted by p_1 , must be defined in the statistical cell model [50,51] of the diluted ternary solutions achieved in binary homogeneous liquids, because the composition of the first solvation shell of the spectrally active molecule can differ from the composition of the liquid mixture in the bulk solution. This parameter is the average percent of the active solvent molecules in the first solvation shell of the solute molecule, which can differ by the molar concentration of this solvent in the bulk solution, noted by x_1 . Relations of the type $p_1 + p_2 = 1$ and $x_1 + x_2 = 1$ are true for the two solvents of ternary solution.

Between these parameters, a linear relation of Type (7) was established [28,32] with the slope near the unity and the cut dependent on the difference $w_2 - w_1$ between the interaction energies in molecular pairs ylid-active solvent (indexed by 1) and ylid-less active solvent (indexed by 2).

$$\ln \frac{p_1}{p_2} = \ln \frac{x_1}{x_2} + \frac{w_2 - w_1}{kT} \quad (7)$$

Relation (7) offers the possibility to estimate the difference $w_2 - w_1$, which is practically impossible to be determined by other methods, except the spectral ones.

The average statistic weight of the active solvent (indexed by 1), p_1 , in the first solute solvation shell can be calculated by using the values of the wavenumbers in the maximum of the ICT band of the spectrally active molecule determined in the binary solutions realized in the two solvents and in the ternary solution, indexed with 1, 2, and t, respectively:

$$p_1 = \frac{v_t - v_2}{v_1 - v_2} \text{ and } p_2 = \frac{v_1 - v_t}{v_1 - v_2} \quad (8)$$

The excess function is as follows:

$$\delta_1 = p_1 - x_1 \quad (9)$$

Reference [50] defines an indicator of the ternary solution non-homogeneity. When $\delta_1 < 0$, the molecules of the inactive solvent (indexed by 2) are predominant in the first solvation shell of the solute. When $\delta_1 > 0$, the molecules of the active solvent are dominant in the solute first solvation shell.

4. Results and Discussion

4.1. Computational Results

PCCM is a pyridinium ylid with symmetrically substituted carbanion having planar structure at the carbanion level. The ylid carbanion is sp_2 hybridized, so the two covalent simple bonds between it and the carbethoxy groups lie in the plane of the heterocycle. The lone electron pair of the carbanion is perpendicular on this plane, facilitating the heterocycle π electrons' conjugation with the electrons belonging to C=O groups of carbethoxy substituents [11].

The Spartan evaluations were made in vacuum, in water, and in ethanol. As one can see from Figure 1, the symmetry of the molecule is not changed in the two hydroxyl solvents, compared with the vacuum structure.

The ground state electric dipole moment of the studied molecule keeps its orientation, parallel to the ylid bond both in water and in ethanol, but changes its absolute value, as it results from the data of Table 1. In the same time, the molecular polarizability does not support significant change when PCCM is passed from vaporous state in solution with water or ethanol (see Table 1).

A significant increase of dipole moment takes place when a PCCM molecule is solvated in water or ethanol, hydroxyl solvents in which hydrogen bond are possible between the ylid carbanion electron lone pair or the electrons of C=O groups and their hydroxyl groups. As seen from Table 1, three places are possible for a hydrogen bond addition to PCCM (three HBA counts are possible for PCCM).

The changes in the E_{HOMO} and E_{LUMO} values listed in Table 1 at passing from vacuum to solutions in water or in ethanol are important because they show us that, in these solvents, the visible band of PCCM will be shifted to blue, which is related to its vaporous state.

The changes in area and volume of PCCM influence the dimensions of the solvation shell of this molecule. The deviation of the molecular structure at sphericity demonstrates that the theories of liquids can be applied only in some approximations, because these theories consider the spectrally active molecules as being spherical entities surrounded by solvent spherical layers.

Let us observe, in Figure 2, some change in the electronic charges near the molecular atoms of PCCM in water or ethanol, compared with vaporous state. The charges located near the atoms component of ylid bond or that at the level of C=O groups of the ylid carbanion are important for the interactions of this molecule with the hydroxyl solvent molecules, as this will result from the solvatochromic analysis.

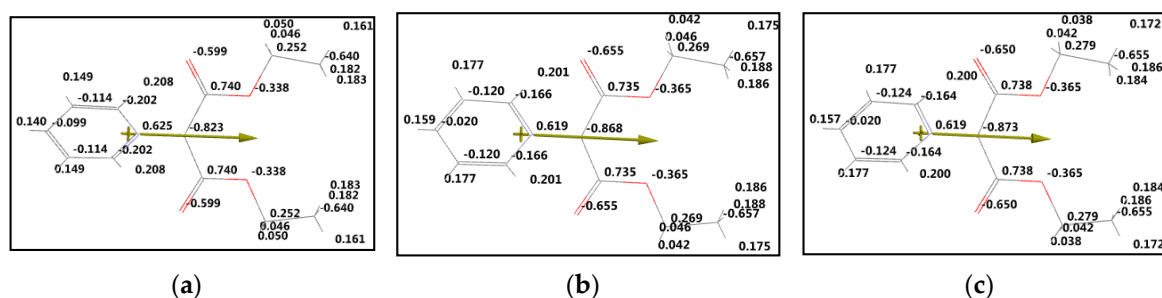


Figure 2. Atomic charges near the atoms of PCCM in (a) vaporous state and in solutions with (b) water and (c) ethanol.

The computational study offers some information about the electron transitions in the visible absorption process, as it results from Figure 3a–c, in which the aspects of the HOMO and LUMO orbitals are illustrated.

The similitude in the orbital aspects in hydroxyl solvents can be observed in Figure 3b,c. All three figures show that, by the visible photon absorption, the heterocycle will be enriched in electron density, thus demonstrating that intramolecular charge transfer (ICT) process takes place from the carbanion and its substituents toward the ylid heterocycle.

An electrostatic potential map (for elucidation the molecular charges distribution), local ionization potential map, and $|LUMO|$ map of PCCM (anticipating the electrophilic and nucleophilic reactivity, respectively) in vaporous phase and in the two hydroxyl solvents are illustrated in Figure 4. Colors in these figures have the signification [28,32] specified below.

The electrostatic map corresponds to the electronic reactivity, providing a measure of the overall size and shape of the molecule. The red color corresponds to high negative potentials, while the blue color indicates high positive potentials.

The electron removing energy as a function of its location is shown by the local ionization potential map. The local ionization potentials are always positive. The blue color indicates large ionization potentials, while the red color corresponds to small ionization potentials.

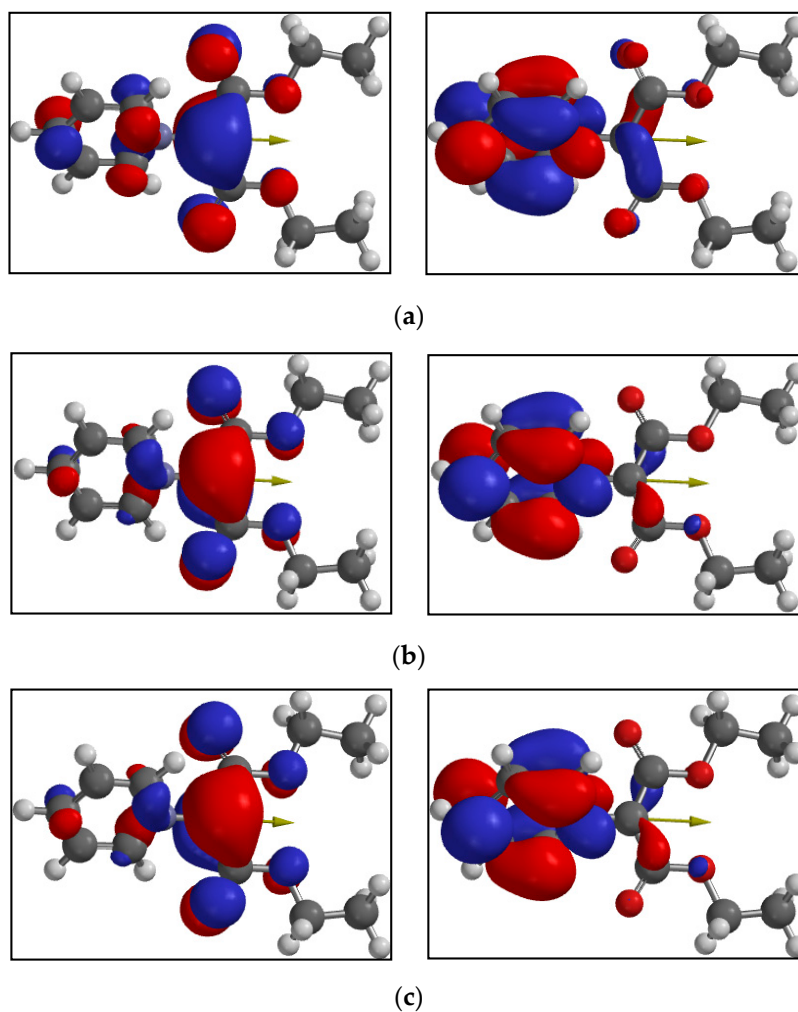


Figure 3. HOMO and LUMO orbitals of PCCM in (a) vaporous state and in solutions with (b) water and (c) ethanol.

The $|LUMO|$ map displays the absolute value of LUMO onto the electron density surface. The red color indicates small absolute values of LUMO, and the blue color shows large absolute values of it.

The places of nucleophilic attack (located near carbanion and near the two oxygens of $C=O$ groups of carboxy substituents) can be observed in Figure 4a–c for PCCM in vaporous phase, or in solutions in water and ethanol, respectively.

The electrostatic potential, local ionization potential and $|LUMO|$ maps keep similar aspects for the vaporous state and also in solutions of PCCM achieved with water and ethanol.

Important for our study are the orientation of the electric dipole moment of PCCM and the aspects of the HOMO and LUMO orbitals, giving information about the sense of the electronic transition in the visible light process and also about the strength of the intermolecular interactions of PCCM in solutions.

The values of the volume and molecular surface area (Table 1) were used to estimate the molecular radius in expressions of the correlation coefficients, C_1 and C_2 , in Relations (4) and (5).

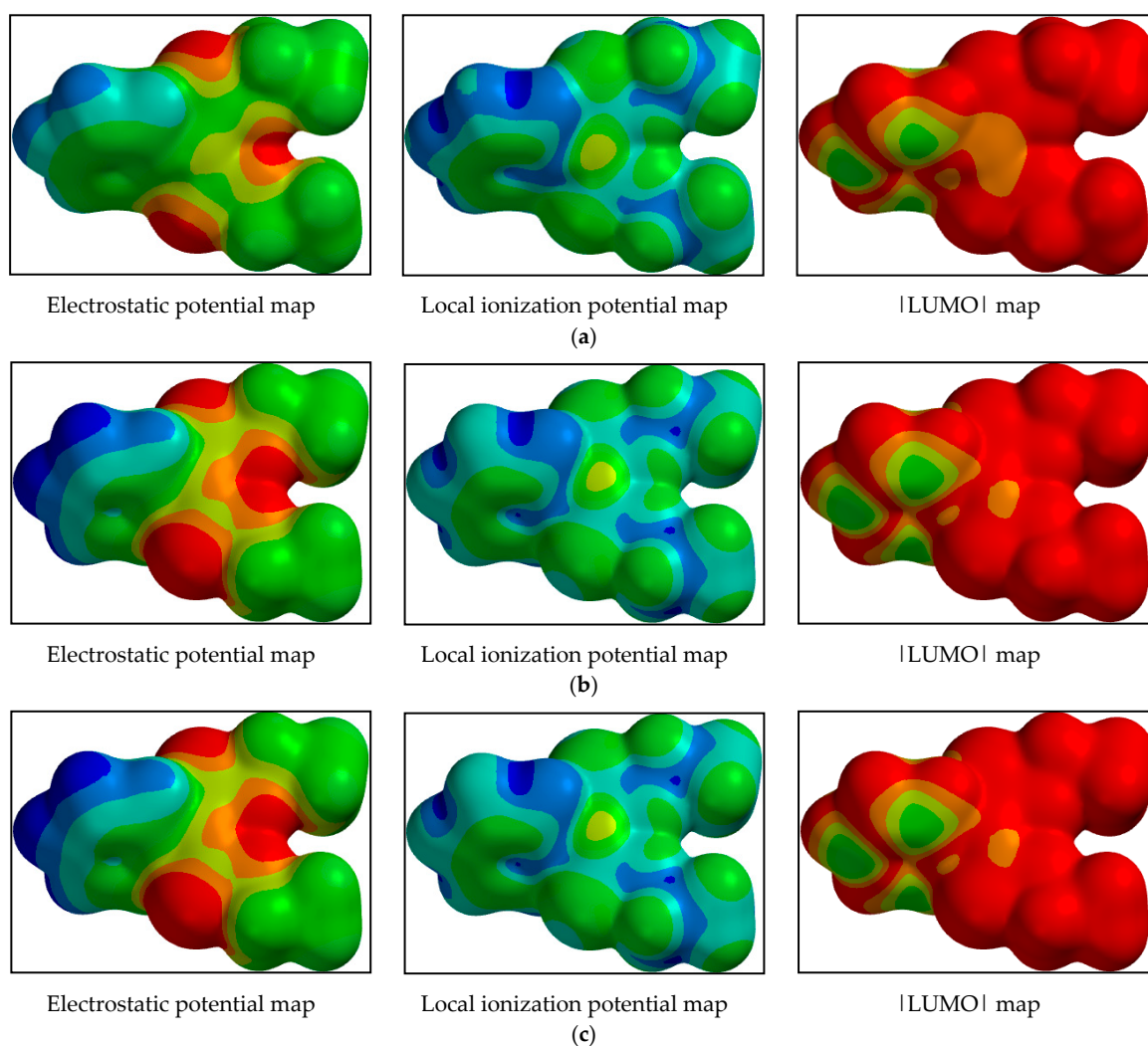


Figure 4. Electrostatic potential map, local ionization potential map, and |LUMO| map of PCCM in (a) vaporous phase, (b) water, and (c) ethanol.

4.2. Spectral Results

PCCM shows a UV region with an intense band attributed to π - π^* transitions and a visible band of small intensity, sensitive to the solvent nature, which disappears in acid media, attributed to n - π^* transition realized by electronic charge transfer from the carbanion towards the ylid heterocycle (see Figures 3 and 5).

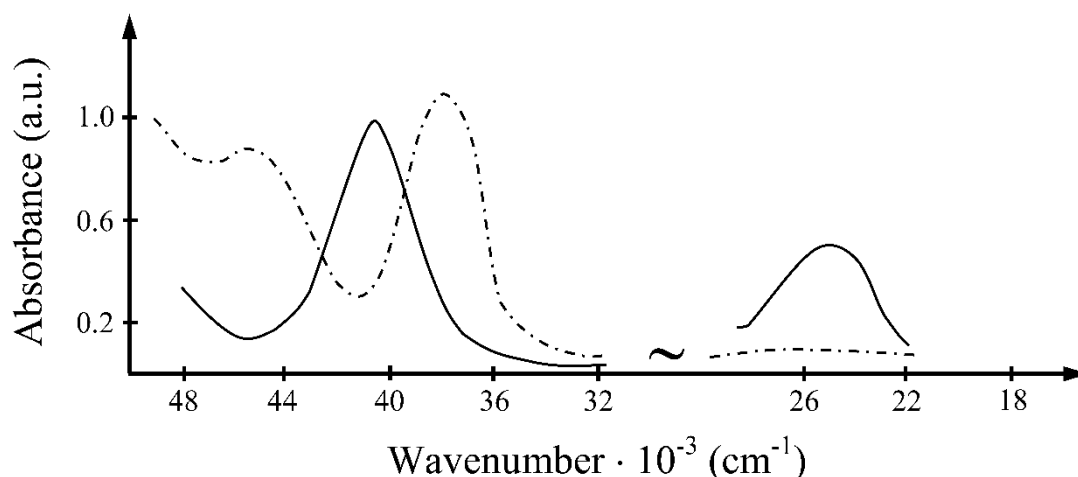


Figure 5. Electronic absorption spectrum of PCCM in ethanol and in ethanol with addition of H₂SO₄. The UV spectrum was recorded by using 0.2 cm quartz cells, and the visible range by using 5 cm glass cells.

The electronic absorption spectrum in ternary solution obtained by adding sulphuric acid in the PCCM solution in ethanol is represented in Figure 5 by a dashed line. The protonated ylid shows spectral changes both in UV and in visible range, as it results from Figure 5. The visible band of PCCM disappears in the acid media in which the lone electron pair of the ylid carbanion is blocked by protonation [11,48].

The spectral data regarding the binary solutions of PCCM are given in Table 2. The solvent parameters are also listed in Table 2. The computed values of the wavenumbers in Table 2 were made by using Relations (10) and (11).

From the data of Table 2, we see the spectral shifts to blue of the visible electronic absorption band both in the polar and in the protic solvents, compared to the non-polar and aprotic ones. Based on the disappearance in acid solutions and on its small intensity, the visible electronic absorption band of PCCM has been attributed to intramolecular charge transfer (ICT) from the carbanion toward the heterocycle [11,24]. This attribution is sustained by the aspects of HOMO and LUMO orbitals (see Figure 3) and by other solvatochromic and computational studies made on similar structures [28,32].

As seen in Table 2, the visible ICT band is very sensitive to the solvent nature and can help us to establish the nature and the strength of interactions between the PCCM molecule and the solvents in diluted solutions.

In order to analyze the solvent effects on the visible electronic absorption band of PCCM, relations of Types (1) and (2) were used.

Based on Kamlet Taft parameters [5,35] of the used solvents (Table 2), the correlation coefficients obtained for Relation (1) in the statistical analysis are listed below.

$$v_{calc.} = (22059 \pm 118) + (1044 \pm 156)\pi^* + (2006 \pm 118)\alpha + (791 \pm 171)\beta \quad (10)$$

Adj. R-square = 0.948, SD = 247 cm⁻¹ and

$$v_{calc.} = (1152 \pm 807) + (0.951 \pm 0.034)v_{exp}, \text{ with: Adj. R-square} = 0.950, \text{ SD} = 235 \text{ cm}^{-1}$$

The dependence between the experimental wavenumbers in the ICT band maximum and those computed by Relation (10) values is illustrated in Figure 6.

The Kamlet Taft solvent parameters were empirically introduced, and they cannot be bonded with the electro-optical parameters of the spectrally active molecules.

For this reason, Relation (2) was also applied to the spectral data given in Table 2, because the correlation coefficients, C₁ and C₂, are expressed as function on the molecular parameters of the spectrally active molecule [28,32] and offer the possibility to characterize the excited state of this

molecule, as it results from Relations (3) and (4). The correlation coefficients obtained based on Relation (2) and the data from Table 2 are listed below. The results of statistical analysis of spectral data based on Relation (11) are illustrated in Figure 7, in which the computed values of the ICT wavenumbers are plotted vs. those experimentally obtained.

$$v_{calc.} = (22026 \pm 419) + (1642 \pm 254)f(\varepsilon) + (-261 \pm 1412)f(n) + (1695 \pm 139)\alpha + (135 \pm 213)\beta \quad (11)$$

Adj. R-square = 0.943, SD = 253 cm⁻¹ and

$$v_{calc.} = (1232 \pm 843) + (0.948 \pm 0.036)v_{exp}, \text{ with: Adj. R-square} = 0.947, \text{ SD} = 237 \text{ cm}^{-1}.$$

Having in view the high values of the errors affecting the correlations coefficients which multiply the solvent parameters $f(n)$ and β , these parameters were eliminated from statistics and the results are the following:

$$v_{calc.} = (21942 \pm 131) + (1731 \pm 212)f(\varepsilon) + (1735 \pm 122)\alpha \quad (12)$$

Adj. R-square = 0.945, SD = 248 cm⁻¹ and

$$v_{calc.} = (1247 \pm 848) + (0.947 \pm 0.036)v_{exp}, \text{ with: Adj. R-square} = 0.946, \text{ SD} = 238 \text{ cm}^{-1}.$$

Table 2. Solvent parameters and wavenumber in the maximum of the visible intramolecular charge transfer (ICT) band of PCCM in binary solutions (experimental, Exp.; computed using Relation (1), Calc. (1), and computed using Relation (2), Calc. (2)).

No.	Solvent	$f(\varepsilon)$	$f(n)$	π^*	β	α	$\tilde{\nu}$ (cm ⁻¹)		
							Exp.	Calc. (1')	Calc. (2'')
1	n-Heptane	0.227	0.240	-0.08	0.00	0.00	22,080	21,975	22,337
2	Dioxane	0.286	0.251	0.55	0.37	0.00	22,900	22,925	22,480
3	Carbon tetrachloride	0.292	0.274	0.28	0.10	0.00	21,910	22,430	22,448
4	Benzene	0.299	0.295	0.59	0.10	0.00	22,550	22,753	22,454
5	p-Xylene	0.299	0.291	0.40	0.13	0.00	22,520	22,602	22,459
6	1,3,5 Trimethylbenzene	0.302	0.293	0.41	0.13	0.00	22,410	22,589	22,463
7	o-Xylene	0.302	0.292	0.41	0.11	0.00	22,450	22,574	22,461
8	Toluene	0.348	0.297	0.54	0.11	0.00	22,720	22,709	22,535
9	Trichloroethylene	0.448	0.282	0.53	0.05	0.00	22,500	22,651	22,695
10	Anisole	0.524	0.302	0.73	0.32	0.00	23,040	23,074	22,851
11	1,2-Dibromoethane	0.538	0.313	0.75	0.00	0.00	22,740	22,841	22,828
12	Chloroform	0.552	0.267	0.69	0.10	0.20	23,280	23,259	23,216
13	n-Butyl acetate	0.577	0.240	0.46	0.45	0.00	23,020	22,895	22,972
14	Iso-amyl acetate	0.589	0.241	0.71	0.07	0.00	23,210	22,855	22,940
15	Chlorobenzene	0.605	0.307	0.71	0.07	0.00	22,950	22,855	22,949
16	Ethyl acetate	0.625	0.228	0.55	0.45	0.00	23,300	22,989	23,054
17	Methyl acetate	0.655	0.221	0.60	0.42	0.00	23,400	23,017	22,101
18	Dichloromethane	0.727	0.256	0.82	0.10	0.20	23,420	23,395	22,506
19	N-Octyl alcohol	0.745	0.258	0.40	0.81	0.77	24,560	24,662	24,597
20	1,2-Dichloroethane	0.752	0.264	0.81	0.10	0.00	23,090	22,983	23,206
21	Pyridine	0.790	0.299	0.87	0.64	0.00	23,100	23,473	23,332
22	N-hexyl alcohol	0.839	0.252	0.04	0.84	0.80	24,520	24,370	24,807
23	Benzyl alcohol	0.804	0.311	0.98	0.52	0.60	24,770	24,697	24,352
24	Cyclohexanol	0.824	0.276	0.45	0.84	0.66	24,600	24,517	24,340
25	N-Amyl alcohol	0.826	0.241	0.40	0.86	0.84	24,350	24,842	24,860
26	N-Butyl alcohol	0.833	0.242	0.47	0.84	0.84	24,550	24,899	24,868
27	Acetophenone	0.833	0.312	0.90	0.49	0.04	23,370	23,466	23,446
28	Iso-Butyl alcohol	0.852	0.239	0.40	0.84	0.69	24,700	24,525	24,646
29	Iso propyl alcohol	0.852	0.234	0.48	0.84	0.76	25,000	24,749	24,646
30	N-Propyl alcohol	0.866	0.239	0.52	0.90	0.84	24,950	24,999	24,931
31	Acetone	0.868	0.222	0.62	0.48	0.08	23,450	23,246	23,594
32	Benzo nitrile	0.889	0.308	0.90	0.37	0.00	23,000	23,291	23,456
33	Ethanol	0.895	0.221	0.86	0.75	0.86	24,970	25,274	24,997
34	Methanol	0.909	0.203	0.60	0.66	0.98	25,230	25,173	25,216
35	Acetonitrile	0.921	0.219	0.75	0.40	0.19	23,750	25,539	23,857
36	DMF	0.924	0.258	0.88	0.69	0.00	23,650	23,523	23,560
37	Ethylene glycol	0.930	0.259	0.90	0.52	0.90	25,560	23,515	25,081
38	DMSO	0.946	0.281	1.00	0.76	0.00	23,720	23,704	23,609
39	1,2,3-Propanetriol	0.948	0.280	0.62	0.51	1.21	25,620	25,536	25,630
40	Water	0.964	0.206	1.09	0.47	1.17	25,430	25,915	25,600
41	Formamide	0.973	0.271	0.97	0.48	0.71	24,190	24,875	24,821

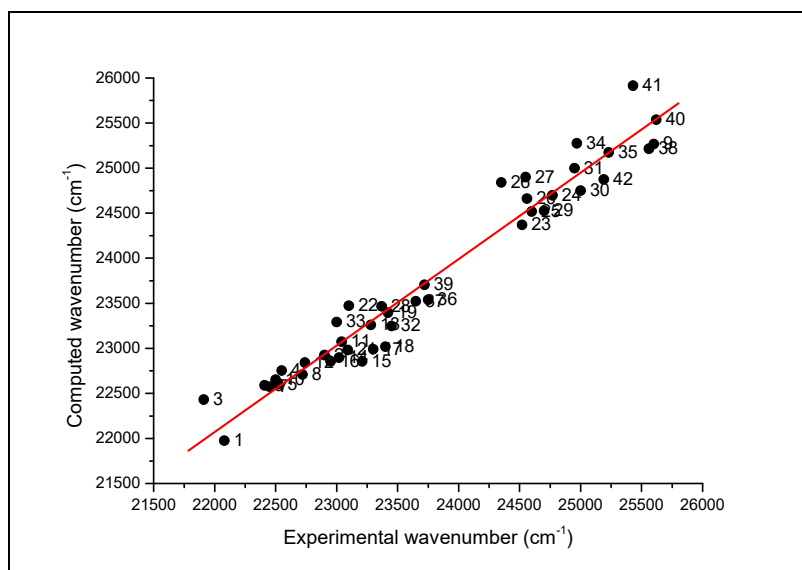


Figure 6. Computed wavenumber with Relation (10) and data from Table 2, v_{calc} (cm^{-1}), vs. experimental wavenumber, v_{exp} (cm^{-1}).

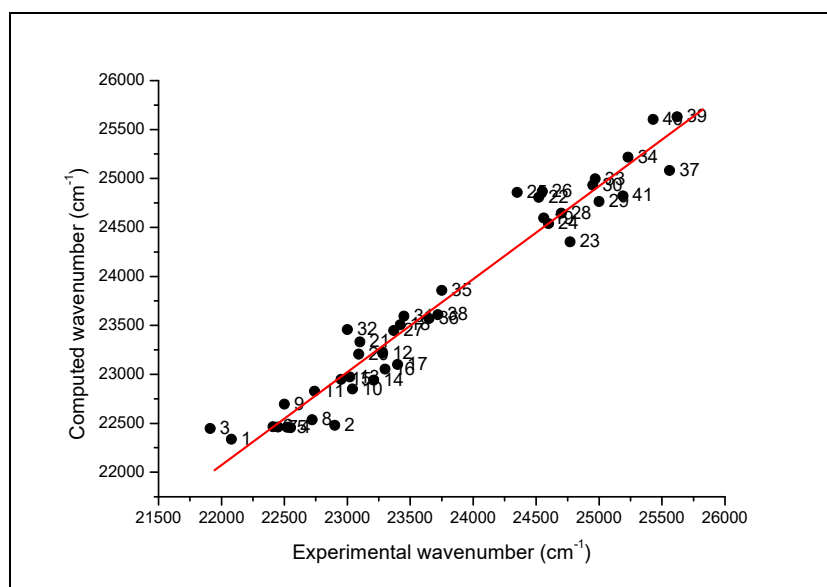


Figure 7. Computed, v_{calc} (cm^{-1}), (with Relation (12')) and data from Table 2) vs. experimental wavenumber, v_{exp} (cm^{-1}).

Relation (12) describes, in a good manner, the dependence of the wavenumber in the maximum of the ICT band of PCCM on the solvent parameters in the binary solutions. The dependence, based on Relation (12), of the computed wavenumbers vs. those experimentally determined for the PCCM binary solutions is illustrated in Figure 7.

The solvatochromic analysis was also made for ternary solutions realized in binary hydroxyl solvents water (1) + ethanol (2) and for water (1) + methanol (2) with the Kamlet Taft solvent parameters from [51]. The solvent parameters and the wavenumbers in the maximum of ICT visible band of PCCM are listed in Tables 3 and 4. The data from Tables 3 and 4 demonstrate that δ_1 (excess function of the active solvent) is positive, that the first solvation shell of PCCM in ternary solutions is enriched in water molecules (water was considered as being the active solvent from the interactions point of view).

Table 3. Binary solvent water (1) + ethanol (2): molar composition (x_1) and Kamlet Taft solvent parameters (π^* , α , β); wavenumbers, ν (cm^{-1}), in the maximum of the PCCM visible ICT band and p_1 .

No.	x_1	π^*	α	β	$\ln \frac{x_1}{x_2}$	PCCM		
						$\vec{\nu}$ (cm^{-1})	p_1	$\ln \frac{p_1}{p_2}$
1	0.000	0.51	0.83	0.98	-	24,970	-	-
2	0.050	0.54	0.83	0.97	-2.94	25,025	0.119	-2.00
3	0.100	0.57	0.84	0.96	-2.20	25,085	0.249	-1.10
4	0.150	0.60	0.83	0.94	-1.74	25,126	0.338	-0.67
5	0.200	0.63	0.83	0.93	-1.39	25,170	0.435	-0.26
6	0.250	0.65	0.83	0.93	-1.10	25,210	0.522	0.09
7	0.300	0.68	0.82	0.92	-0.85	25,245	0.599	0.40
8	0.350	0.70	0.81	0.91	-0.62	25,275	0.663	0.68
9	0.400	0.73	0.80	0.91	-0.41	25,315	0.750	1.10
10	0.450	0.75	0.79	0.89	-0.20	25,335	0.792	1.34
11	0.500	0.77	0.79	0.90	0.00	25,360	0.848	1.72
12	0.550	0.80	0.78	0.89	0.20	25,370	0.870	1.90
13	0.600	0.82	0.77	0.89	0.41	25,380	0.891	2.10
14	0.650	0.85	0.77	0.89	0.62	25,385	0.902	2.22
15	0.700	0.90	0.74	0.88	0.85	25,390	0.913	2.35
16	0.750	0.94	0.71	0.86	1.10	25,400	0.935	2.67
17	0.800	1.00	0.67	0.87	1.39	25,408	0.952	2.99
18	0.825	1.03	0.66	0.87	1.55	25,410	0.957	3.10
19	0.850	1.06	0.64	0.90	1.74	25,413	0.963	3.26
20	0.875	1.09	0.61	0.92	1.95	25,415	0.967	3.38
21	0.900	1.11	0.59	0.97	2.20	25,420	0.978	3.79
22	0.925	1.12	0.56	1.03	2.51	25,422	0.983	4.06
23	0.950	1.13	0.54	1.11	2.94	25,425	0.989	4.50
24	0.975	1.13	0.52	1.18	3.66	25,428	0.996	5.52
25	1.000	1.13	0.50	1.26	-	25,430	-	-

Table 4. Binary solvent water (1) + methanol (2): solvent molar composition (x_1) and Kamlet Taft solvent parameters (π^* , α , β); wavenumbers ν (cm^{-1}) in the maximum of the PCCM visible ICT band and p_1 .

No.	x_1	π^*	α	β	$\ln \frac{x_1}{x_2}$	PCCM		
						$\vec{\nu}$ (cm^{-1})	p_1	$\ln \frac{p_1}{p_2}$
1	0.000	0.58	0.74	1.14	-	25,190	-	-
2	0.050	0.61	0.74	1.13	-2.94	25,201	0.046	-3.03
3	0.100	0.64	0.74	1.12	-2.20	25,225	0.146	-1.77
4	0.150	0.66	0.74	1.10	-1.74	25,250	0.249	-1.10
5	0.200	0.70	0.74	1.09	-1.39	25,270	0.334	-0.69
6	0.250	0.73	0.74	1.07	-1.10	25,285	0.397	-0.42
7	0.300	0.76	0.74	1.06	-0.85	25,313	0.512	0.05
8	0.350	0.78	0.72	1.04	-0.62	25,330	0.584	0.34

Table 4. Cont.

No.	x_1	π^*	α	B	$\ln \frac{x_1}{x_2}$	PCCM		
						$\vec{\nu}$ (cm ⁻¹)	p_1	$\ln \frac{p_1}{p_2}$
9	0.400	0.82	0.72	1.04	−0.41	25,350	0.666	0.69
10	0.450	0.85	0.71	1.02	−0.20	25,365	0.729	0.99
11	0.500	0.88	0.70	1.03	0.00	25,375	0.770	1.21
12	0.550	0.91	0.68	1.02	0.20	25,385	0.813	1.47
13	0.600	0.95	0.66	1.01	0.41	25,390	0.833	1.61
14	0.650	0.98	0.65	1.01	0.62	25,401	0.879	1.98
15	0.700	1.01	0.63	1.01	0.85	25,408	0.908	2.29
16	0.750	1.04	0.61	1.02	1.10	25,415	0.938	2.72
17	0.800	1.06	0.59	1.06	1.39	25,420	0.958	3.13
18	0.825	1.08	0.58	1.07	1.55	25,422	0.967	3.38
19	0.850	1.09	0.56	1.09	1.74	25,424	0.975	3.66
20	0.875	1.10	0.55	1.12	1.95	25,425	0.979	3.84
21	0.900	1.11	0.54	1.13	2.20	25,426	0.983	4.06
22	0.925	1.11	0.52	1.17	2.51	25,427	0.988	4.41
23	0.950	1.12	0.52	1.19	2.94	25,428	0.992	4.82
24	0.975	1.12	0.51	1.22	3.66	25,430	-	-
25	1.000	1.14	0.49	1.23	-	25,430	-	-

The dependence of Type (1) was observed for the ternary PCCM solutions in both pairs of binary solvents. The correlation coefficients obtained using Relation (1) and the data from Tables 3 and 4 for the two types of solutions are given in Relations (13) and (14). The dependence between the computed, ν_{calc} (cm⁻¹) and the experimental wavenumber, ν_{exp} (cm⁻¹), and for PCCM in water (1) + ethanol (2) and in water (1) + methanol (2) is illustrated in Figures 8 and 9.

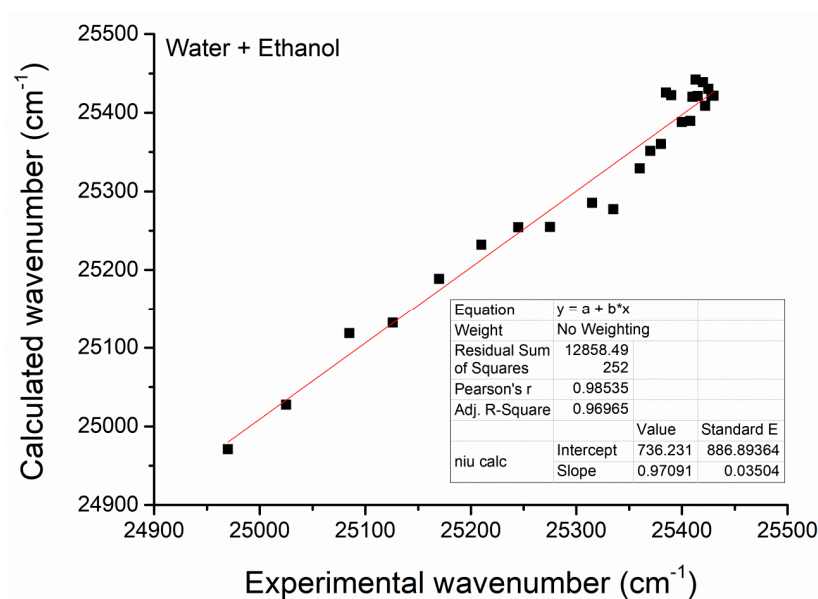


Figure 8. Computed wavenumber, ν_{calc} (cm⁻¹) (with Relation (13) and data from Table 3), vs. experimental wavenumber, ν_{exp} (cm⁻¹) for ternary solution PCCM + water + ethanol.

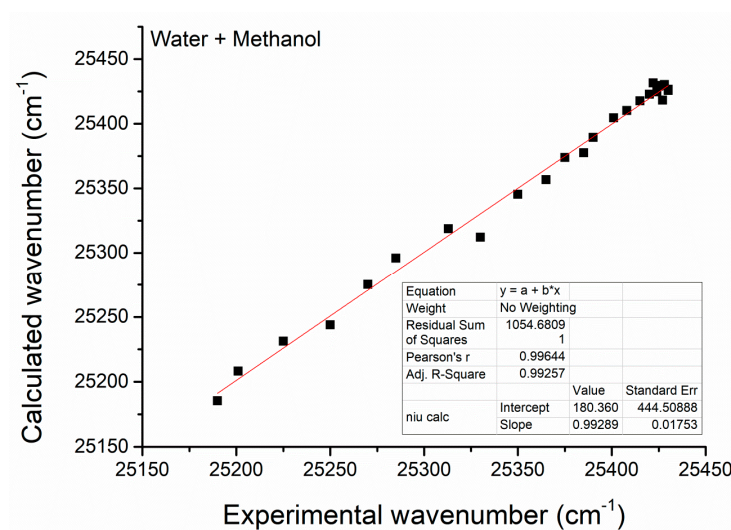


Figure 9. Computed wavenumber, v_{calc} (cm^{-1}), (with Relation (14) and data from Table 4), vs. experimental wavenumber, v_{exp} (cm^{-1}) for ternary solution PCCM + water + methanol.

The presence of some aberrant points for high water content in Figure 8 could be explained [52] by the increased ability of water to make some cages around the hydrocarbon part of superior alcohols. This ability increases with the length of hydrocarbon chain from the alcohol molecules, and it was emphasized for water + ethanol mixtures [51].

Results for ternary solution PCCM in water (1) + ethanol (2):

$$v_{calc.} = (20153 \pm 533) + (2174 \pm 165)\pi^* + (3451 \pm 367)\alpha + (862 \pm 145)\beta \quad (13)$$

Adj. R-square = 0.967

$$v_{calc.} = (736 \pm 886) + (0.971 \pm 0.035)v_{exp.}, \text{ with: Adj. R-square} = 0.950, \text{ SD} = 235 \text{ cm}^{-1}$$

Results for solution PCCM in water (1) + methanol (2):

$$v_{calc.} = (23772 \pm 817) + (827 \pm 62)\pi^* + (961 \pm 148)\alpha + (194 \pm 71)\beta \quad (14)$$

Adj. R-square = 0.992

$$v_{calc.} = (180 \pm 445) + (0.993 \pm 0.018)v_{exp.}, \text{ with: Adj. R-square} = 0.993, \text{ SD} = 100 \text{ cm}^{-1}$$

The contribution of each type of intermolecular interaction in PCCM diluted solutions can be estimated based on the data from Tables 2–4 and the values of the correlation coefficients established in statistical analysis. As it results from the linear dependences expressed in Figures 6–8, in PCCM, diluted binary and ternary solutions act both universal and specific interactions.

The universal interactions of the orientation–induction type are dominant in aprotic solvents, while, in the hydroxyl solvents, a great contribution to the spectral shift of ICT visible band of PCCM is given by specific interactions between the ylid and the hydroxyl groups of these solvents (see Tables 5 and 6).

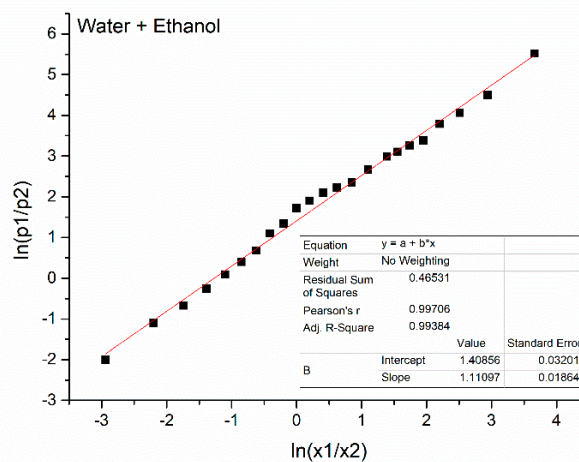
The dependence of the type $\ln \frac{p_1}{p_2}$ vs. $\frac{x_1}{x_2}$, where p_1 and x_1 are the statistic average weight of the active solvent (considered by us as being water) in the first solvation shell of PCCM and the molar fraction of the same solvent in the bulk solution, respectively, for PCCM ternary solutions is illustrated in Figures 10 and 11. The index 2 shows the same parameters for the second solvent, considered as being a few active from the interactions point of view.

Table 5. Contribution of each type of intermolecular interactions (in binary solutions) to the spectral shifts of PCCM visible ICT band.

No.	Solvent	$C_1f(\epsilon)$ (cm^{-1})	p_1 (%)	$C_2f(n)$ (cm^{-1})	p_2 (%)	$C_3\alpha$ (cm^{-1})	p_3 (%)	$C_4\beta$ (cm^{-1})	p_4 (%)
1	n-Heptane	372.7	85.6	62.6	14.4	0.0	0.0	0.0	0.0
2	Dioxane	469.6	80.3	65.5	11.2	0.0	0.0	49.8	8.5
3	Carbon tetrachloride	479.4	85.0	71.5	12.7	0.0	0.0	13.5	2.4
4	Benzene	490.9	84.5	76.9	13.2	0.0	0.0	13.5	2.3
5	p-Xylene	490.9	84.0	75.9	13.0	0.0	0.0	17.5	3.0
6	1,3,5-Trimethylbenzene	495.9	84.1	76.4	13.0	0.0	0.0	17.5	3.0
7	o-Xylene	495.9	84.5	76.1	13.0	0.0	0.0	14.8	2.5
8	Toluene	571.4	86.1	77.5	11.7	0.0	0.0	14.8	2.2
9	Trichloroethylene	735.6	90.2	73.5	9.0	0.0	0.0	6.7	0.8
10	Anisole	860.4	87.6	78.8	8.0	0.0	0.0	43.1	4.4
11	1,2-Dibromoethane	883.4	91.5	81.6	8.5	0.0	0.0	0.0	0.0
12	Chloroform	906.3	68.2	69.6	5.2	339.0	25.5	13.5	1.0
13	n-Butyl acetate	947.4	88.5	62.6	5.8	0.0	0.0	60.6	5.7
14	Iso-amyl acetate	967.1	93.0	62.8	6.0	0.0	0.0	9.4	0.9
15	Chlorobenzene	993.4	91.7	80.1	7.4	0.0	0.0	9.4	0.9
16	Ethyl acetate	1026.2	89.5	59.5	5.2	0.0	0.0	60.6	5.3
17	Methyl acetate	1075.5	90.4	57.6	4.8	0.0	0.0	56.5	4.8
18	Dichloromethane	1193.7	74.0	66.8	4.1	339.0	21.0	13.5	0.8
19	N-Octyl alcohol	1223.2	45.2	67.3	2.5	1305.2	48.3	109.0	4.0
20	1,2-Dichloroethane	1234.7	93.8	68.8	5.2	0.0	0.0	13.5	1.0
21	Pyridine	1297.1	88.8	78.0	5.3	0.0	0.0	86.1	5.9
22	N-hexyl alcohol	1377.6	47.3	65.7	2.3	1356.0	46.6	113.0	3.9
23	Benzyl alcohol	1320.1	53.1	81.1	3.3	1017.0	40.9	70.0	2.8
24	Cyclohexanol	1353.0	50.9	72.0	2.7	1118.7	42.1	113.0	4.3
25	N-Amyl alcohol	1356.2	45.8	62.8	2.1	1423.9	48.1	115.7	3.9
26	N-Butyl alcohol	1367.7	46.1	63.1	2.1	1423.9	48.0	113.0	3.8
27	Acetophenone	1367.7	86.4	81.4	5.1	67.8	4.3	65.9	4.2
28	Iso-Butyl alcohol	1398.9	51.0	62.3	2.3	1169.6	42.6	113.0	4.1
29	Iso propyl alcohol	1398.9	48.9	61.0	2.1	1288.2	45.0	113.0	4.0
30	N-Propyl alcohol	1421.9	46.9	62.3	2.1	1423.9	47.0	121.1	4.0
31	Acetone	1425.2	84.7	57.9	3.4	135.6	8.1	64.6	3.8
32	Benzo nitrile	1459.7	91.8	80.3	5.1	0.0	0.0	49.8	3.1
33	Ethanol	1469.5	47.6	57.6	1.9	1457.8	47.2	100.9	3.3
34	Methanol	1492.5	45.3	52.9	1.6	1661.2	50.4	88.8	2.7
35	Acetonitrile	1512.2	77.7	57.1	2.9	322.1	16.6	53.8	2.8
36	DMF	1517.1	90.5	67.3	4.0	0.0	0.0	92.9	5.5
37	Ethylene glycol	1527.0	47.9	67.5	2.1	1525.6	47.8	70.0	2.2
38	DMSO	1553.3	89.8	73.3	4.2	0.0	0.0	102.3	5.9
39	1,2,3-Propanetriol	1556.5	41.5	73.0	1.9	2051.0	54.7	68.6	1.8
40	Water	1582.8	43.0	53.7	1.5	1983.2	53.8	63.2	1.7
41	Formamide	1597.6	54.4	70.7	2.4	1203.5	41.0	64.6	2.2

Table 6. Contribution (in percents) of each type of intermolecular interaction to the spectral shift in PCCM ternary solutions.

No.	x_1	Water + Ethanol				Water + Methanol			
		$\Delta\bar{\nu}$ (cm^{-1})	$C_1\pi^*$ %	$C_2\alpha$ %	$C_3\beta$ %	$\Delta\bar{\nu}$ (cm^{-1})	$C_1\pi^*$ %	$C_2\alpha$ %	$C_3\beta$ %
1	0.000	4817	23.0	59.5	17.5	1417	33.9	50.3	15.8
2	0.050	4872	24.0	58.8	17.2	1428	35.5	49.9	15.6
3	0.100	4932	25.0	58.5	16.5	1452	35.5	49.2	15.3
4	0.150	4973	26.1	57.6	16.3	1477	37.0	48.3	14.7
5	0.200	5017	27.0	57.0	16.0	1497	38.7	47.3	14.0
6	0.250	5057	28.0	56.6	15.4	1512	39.9	47.2	13.9
7	0.300	5092	27.8	55.6	15.6	1540	40.8	46.2	13.0
8	0.350	5122	29.7	55.0	15.3	1557	41.4	45.5	13.1
9	0.400	5162	30.8	54.0	15.2	1577	43.0	43.9	13.1
10	0.450	5182	31.6	53.6	14.8	1592	44.2	42.8	13.0
11	0.500	5207	32.3	52.8	14.9	1602	45.4	42.0	12.6
12	0.550	5217	33.7	51.6	14.7	1612	46.7	40.8	12.5
13	0.600	5227	34.5	50.8	14.7	1617	48.6	39.2	12.2
14	0.650	5232	35.4	50.8	14.8	1628	49.8	38.2	12.0
15	0.700	5237	37.4	47.8	14.8	1635	51.0	37.0	12.00
16	0.750	5247	39.2	46.7	14.1	1642	52.4	35.6	12.0
17	0.800	5255	41.5	44.1	14.4	1647	53.1	34.4	12.5
18	0.825	5257	42.6	43.2	14.2	1649	54.0	33.8	12.2
19	0.850	5260	43.8	42.0	14.2	1651	54.6	32.6	12.8
20	0.875	5262	45.0	40.0	15.0	1652	55.0	32.0	13.0
21	0.900	5267	45.8	38.7	15.5	1653	55.5	31.4	13.1
22	0.925	5269	46.4	36.7	16.9	1654	55.5	30.6	13.9
23	0.950	5272	46.6	35.4	18.0	1655	56.0	30.0	14.0
24	0.975	5275	46.6	34.0	19.4	1657	55.9	29.7	14.4
25	1.000	5277	23.0	59.5	17.53	46.6	32.7	20.7	

**Figure 10.** $\ln \frac{p_1}{p_2}$ vs. $\ln \frac{x_1}{x_2}$ for ternary for ternary solution PCCM + water (1) + ethanol (2).

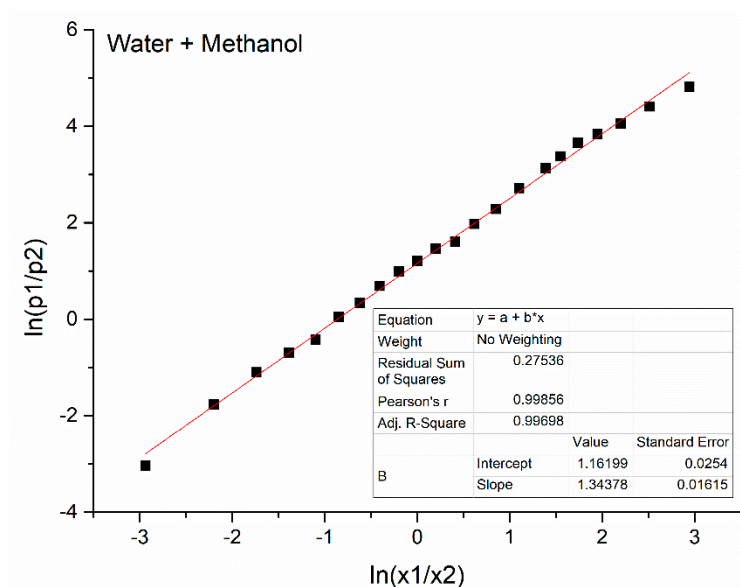


Figure 11. $\ln \frac{p_1}{p_2}$ vs. $\ln \frac{x_1}{x_2}$ for ternary solution PCCM + water (1) + methanol (2).

From Figures 10 and 11, it results a linear dependence between the points corresponding to both types of the binary hydroxyl solvents, proving the applicability of the statistic cell model of ternary solutions to the studied mixtures.

The difference between the interaction energies in the molecular pairs of the types PCCM–water (1) and PCCM–ethanol (2) and, respectively, PCCM–Water (1) and PCCM–Methanol (2) was estimated based on the significance of the cut at origin of the corresponding lines (see Figures 10 and 11).

The difference $w_2 - w_1$, determined using the cut of line (7) for the ternary solution PCCM + water (1) + ethanol (2), has the value $w_2 - w_1 = (0.574 \pm 0.013)10^{-20}J$, and for solution PCCM + water (1) + methanol (2) has the value $w_2 - w_1 = (0.475 \pm 0.010)10^{-20}J$. These values demonstrate (by their positive signs) that the interaction energy of ylid molecule with a water molecule is higher in modulus compared with those between the ylid and one alcohol molecule (either ethanol or methanol).

The difference $w_2 - w_1$ is higher for the case of ternary solutions in water + ethanol, proving that the interaction energy in molecular pairs: ylid–ethanol is smaller compared with that corresponding to pairs: ylid–methanol.

A study of the protic solvent influence on the visible ICT band of pyridinium di-carbethoxy methylid and of iso-quinolinium di-carbethoxy methylid was also accomplished in Reference [27]. The difference $w_2 - w_1$ was estimated for the binary solvents containing one protic and one aprotic solvent. The $w_2 - w_1$ values obtained in Reference [27] for pyridinium di-carbethoxy methylid were $0.289 \cdot 10^{-20}J$ for the binary solvent octanol (1) + dichloroethane (2) and $0.190 \cdot 10^{-20}J$ for the binary solvent methanol (1) + benzene (2).

The higher values obtained in this paper for binary solvents containing water and ethanol or methanol, compared with those obtained in Reference [27], could be explained by the action of the orientation–induction forces on the complexes formed by ylid with hydroxyl molecule, having in view the high value of the water electric permittivity. A study of the orientation–induction interactions in ternary solutions pyridinium ylids + water + ethanol has been made in Reference [53,54] and emphasized the great contribution of the orientation interactions on the ylid complexes realized by hydrogen bonds.

The experimental data regarding the interactions between two molecules are important for the researchers who study the interactions in liquids, because there are few methods in which these types of data can be obtained (any of the devices introduced in liquids for measurements disturb the internal equilibrium in this state of matter). Only spectrally active molecules are used as probes able to estimate, by spectra modifications, the strength of the reactive internal field in liquids.

Information about the excited states of the spectrally active molecules, especially about their excited electric dipole moment and its orientation relative to the ground state dipole moment are important for quantum chemistry and can serve to develop the calculations in the molecular excited states.

The dipole moment of PCCM in its first excited state (corresponding to the ICT process caused by the visible photon absorption) is estimated here by using the variational method proposed in Reference [28,32,41] and the data of PCCM in the ground state obtained in quantum chemical estimation (Table 1).

With the values of the correlation coefficients, C_1 and C_2 , obtained in (11) based on Relations (3) and (4) and using the computed by Spartan'14 values of the ground state electric dipole moment and polarizability of PCCM, the variational method proposed in Reference [41] permitted us to estimate the excited state dipole moment of PCCM and the angle between the dipole moments in the electronic state between which the absorption transition takes place, in the approximation that the molecular polarizability does not vary in the electronic transition time [2,34].

Let us apply this method for the PCCM by using the data from Table 1, the values of the coefficients, C_1 and C_2 , from Relation (11), and the molecular radius computed by using the surface area and volume in Formula (6).

The estimation is made in some approximations, having in view the ovality of PCCM molecule obtained by Spartan (see Table 1) and the hypothesis of the cell model regarding the solute and solvation shell sphericity. Using Definitions (4) and (5) and the values of the coefficients, C_1 and C_2 , one obtains the following:

$$\alpha_e = 64.3783 - 0.1168\mu_e^2 \quad (15)$$

$$0.0143\mu_e^2 - 12.56\mu_e \cos \varphi + 72.1007 = 0 \quad (16)$$

Equations (15) and (16) were obtained by using the values for the sum $C_1 + C_2$ and C_1 regression coefficients from Relation (11) and the ground state dipole moment of PCCM computed in water (Table 1).

Equation (16) has real solutions in the hypothesis that its discriminator is a positive quantity. A limitation for the angle, φ , between the dipole moments results in this condition.

$$\varphi \in [0, 80.69] \cup (99.31, 180]^\circ \quad (17)$$

The excited state dipole moment, obtained as the real solution of Equation (16), is used for estimating the excited state polarizability of PCCM based on Relation (15).

In variational method, the angle between the molecular dipole moments in the electronic states participating to the absorption process is varied until the polarizability in the excited state of the spectrally active molecule equalizes the ground state polarizability. In conformity with the supposition of McRae [2], the electronic transition takes place for the corresponding value of the angle, φ . The data are listed in Table 7.

Table 7. Excited state dipole moment and polarizability for different angles, φ .

No.	Φ (Degree)	μ_e (D)	α_e (cm ³)
1	0	5.778	60.48
2	5	5.801	60.45
3	8	5.837	60.40
4	8.5	5.842	60.39
5	8.6	5.845	60.388
6	9	5.853	70.37

In Table 7, only some of the estimations are listed, because for $\varphi = 8.5^\circ$, the value of the excited state polarizability equalizes the ground state polarizability, and one can appreciate that the electronic transition with ICT takes place at this angle. The results obtained when the dipole moments triangle (Figure 12) was solved are $\mu_e = 5.84D$, $\Delta\mu = 1D$, $\varphi = 8.5^\circ$, for initial values $\mu_g = 6.28D$, computed by Spartan for PCCM in water; $I_u = 5.58$ eV and $I_v = 9.96$ eV (for cyclohexane); and $C_1 = 1642$ cm⁻¹ and $C_2 = -261$ cm⁻¹. In Figure 12, the angle between the ground state dipole moment and the vector $\Delta\mu$ is 59.72 degrees, and the angle between the excited state dipole moment and the vector $\Delta\mu$ is 111.78 degrees.

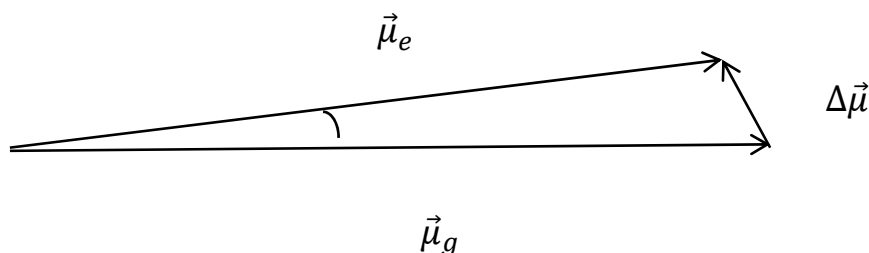


Figure 12. Triangle of the dipole moments for visible ICT transition of PCCM.

In the case when only $f(\epsilon)$ and α influence the wavenumber in the maximum of the ICT band (see Relation (12')), the correlation coefficients are $C_1 = 1731$ cm⁻¹ and $C_2 = 0$ cm⁻¹. A system of equations of the Types (18) and (19) is obtained in this case.

$$\alpha_e = 64.2213 - 0.1168\mu_e^2 \quad (18)$$

$$0.0143\mu_e^2 - 12.56 \mu_e \cos \varphi + 71.7802 = 0 \quad (19)$$

Equations (18) and (19) have the solutions as it follows.

The real solutions are obtained for $\varphi \in [0, 80.71) \cup (99.28, 180]^\circ$, but the condition that the excited state polarizability is the same as in the ground electronic state imposes the following solutions: $\varphi = 0^\circ$, $\mu_e = 5.75D$, and $\Delta\mu = 0.53D$. The parallelism between the ground and excited dipole moments of the molecule in the time of ICT can be admitted with good precision, having in view the approximation in which the theory regarding the solvent influence on the wavenumbers of the electronic transitions in the absorption process has been developed.

In the case of symmetrically substituted carbanion, the angle between the dipole moments process is small, and the excited state dipole moment is smaller than the ground state dipole moment. This fact determines the hypsochromic shift of the ICT band in polar solvents, because the solvation energy of the orientation induction type is higher in the ground state of PCCM molecule, compared with that in its excited state.

5. Conclusions

The experimental data obtained in solvatochromic study and quantum mechanical parameters computed by Spartan can be used in order to characterize the excited electronic state of a spectrally active molecule without fluorescence spectrum.

The excited state dipole moment of PCCM in the excited state of the ICT transition, estimated here by the variational method, is smaller than the ground state dipole moment, and it makes a small angle with this.

The long-range (universal) interactions of the dipolar types of PCCM with the solvents are stronger in the ground electronic state, as compared with the excited state.

The universal interactions are predominant in PCCM solutions achieved in aprotic solvents, while in the protic ones, the specific interactions of the hydrogen types in which the ylid molecules accept protons significantly influence the position of the visible ICT band of ylid.

A part of experimental data obtained in this research could be used by researchers in the quantum chemistry field for developing quantum chemical computations for the excited state parameters of the ylid molecules in different liquids.

Author Contributions: Spectral studies in binary and ternary solutions, D.O.D., D.E.C., D.G.D., and G.G.M.; computational studies of PCCM molecule in vacuum, in water and in ethanol, by SPARTAN 14, A.C.M., A.G.-T., and C.C.; chemical reactions and analyses, N.P.M. and E.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Onsager, L. Electric moments of molecules in liquids. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493. [CrossRef]
2. McRae, E.G. Theory of solvent influence on the molecular electronic spectra. Frequency shifts. *J. Phys. Chem.* **1957**, *61*, 562–572. [CrossRef]
3. Bakhshiev, N.G. *Spectroscopy of Intermolecular Interactions*; Nauka: St. Petersburg, Russian, 1972. (In Russian)
4. Abe, T. Theory of solvent influence on the molecular electronic spectra. Frequency shifts. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1314–1318. [CrossRef]
5. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.
6. Dorohoi, D.O.; Holban, V. Intermolecular interactions in some pyridazinium ylids solutions. *J. Mol. Struct.* **1993**, *293*, 133–136. [CrossRef]
7. Kowski, A. Ground and excited state dipole moments of 6-propionyl-2-(dimethyl amino)-naphthalene determined by solvatochromic shifts. *Z. Naturforsch* **1999**, *54*, 379–381. [CrossRef]
8. Zakerhamidi, M.S.; Moghadam, M.; Ghanadzadeh, A.; Hosseini, S. Anisotropic and isotropic solvent effects on the dipole moment and photophysical properties of rhodamine dyes. *J. Lum.* **2012**, *132*, 931–937. [CrossRef]
9. Stanculescu, E.R.; Stroia, L.; Dorohoi, D.O. Solvatochromism Used in Determining Some Electro-Optical Parameters. Proceedings SPIE nr. 8001, 2011, nr. Art. 80012S, Published in 2011. Available online: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/8001/80012S/Solvatochromism-used-in-determining-some-molecular-electro-optical-parameters/10.1117/12.891949.short> (accessed on 20 June 2020).
10. Ivan, L.M.; Dimitriu, D.G.; Gritco-Todirascu, A.; Morosanu, A.C.; Dorohoi, D.O.; Cheptea, C. Excited state dipole moments of two pyridazinium p-nitro-phenacylids estimated from solvatochromic study. *Spectrosc. Lett.* **2020**, *53*, 1–11. [CrossRef]
11. Zugravescu, I.; Petrovanu, M. *N-Ylid Chemistry*; Academic Press: New York, NY, USA, 1976.
12. Beak, P.; Reitz, D.B. Dipole stabilized carbanions: Novel and useful intermediates. *Chem. Rev.* **1978**, *78*, 275–316. [CrossRef]
13. Radzhabov, M.R.; Tsyganov, D.V.; Pivina, T.S.; Krayushkin, M.M.; Seeboth, N.; Ivanov, S.; Frederique-Salit, A. Syntheses of pyridinium ylids and simulation of their 1, 3 dipolar Cycloaddition mechanism. *Mendeleev Commun.* **2017**, *27*, 503–505. [CrossRef]
14. Jacobs, J.; van Hende, E.; Claessens, S.; De Kimpe, N. Pyridinium ylids in heterocyclic synthesis. *Curr. Org. Chem.* **2011**, *15*, 1340–1362. [CrossRef]
15. Pawda, A.; Austin, D.J.; Percedo, L.; Lin, Z. Cycloaddition reactions of pyridinium and related azomethine ylides. *J. Org. Chem.* **1993**, *58*, 1144–1150. [CrossRef]
16. Allgäuer, D.S.; Mayer, P.; Mayr, H. Nucleophilicity parameters of pyridinium ylides and their use in mechanistic analyses. *J. Am. Chem. Soc.* **2013**, *135*, 15216–15224. [CrossRef] [PubMed]
17. Bonte, S.; Ghenea, I.O.; Dinica, R.; Baussanne, I.; Demeunynck, M. Investigation of the pyridinium ylide-alkene Cycloaddition as a fluorogenic coupling reaction. *Molecules* **2016**, *21*, 332. [CrossRef] [PubMed]
18. Albrecht, M.; Yulikov, M.; Kohn, T.; Jeschke, G. Pyridinium salts and ylides as partial structures of photoresponsive Merrifield resins. *J. Mat. Chem.* **2010**, *20*, 3025–3034. [CrossRef]
19. Schwalm, R.; Bottcher, A.; Koch, H. MID UV resistant materials containing pyridinium ylides. *Proc. SPIE* **1988**. [CrossRef]

20. Streith, J. The photochemistry of N-iminopyridinium ylides in retrospect. From a simple concept to same applications. *CHIMIA* **1991**, *45*, 65–76.
21. Taylor, L.D.; Karl, M.; Haubs, J. *Polymeric Pyridinium Ylide and Products from Same*; European Patent Office: Munich, Germany, 1985.
22. Leontie, L.; Olariu, I.; Rusu, I.G. On the charge transport in some new carbanion disubstituted in thin films. *Mater. Chem. Phys.* **2003**, *80*, 506–511. [[CrossRef](#)]
23. Leontie, L.; Roman, M.; Branza, F.; Podaru, C.; Rusu, I.G. Electrical and optical properties of some new synthesized ylides in thin films. *Synth. Mat.* **2003**, *138*, 157–163. [[CrossRef](#)]
24. Dorohoi, D.O. Electronic spectroscopy of N-ylids. *J. Mol. Struct.* **2004**, *704*, 31–43. [[CrossRef](#)]
25. Pop, V.; Dorohoi, D.O.; Holban, V. Molecular interactions in binary solutions of 4-aminophthalimide and 3p-cumyl-pyridazinium acetyl benzoyl methylid. *Spectrochim. Acta A* **1994**, *50*, 2281–2289. [[CrossRef](#)]
26. Dorohoi, D.O.; Partenie, H.D. The Spectroscopy of N-ylids. *J. Mol. Struct.* **1993**, *293*, 129–132. [[CrossRef](#)]
27. Gheorghies, C.; Gheorghies, L.V.; Dorohoi, D.O. Solvent influence on some complexes realized by Hydrogen bond. *J. Mol. Struct.* **2008**, *887*, 122–127. [[CrossRef](#)]
28. Morosanu, A.C.; Gritco Todirascu, A.; Creanga, D.E.; Dorohoi, D.O. Computational and solvatochromic study of pyridinium acetyl benzoyl methylid (PABM). *Spectrochim. Acta A* **2018**, *189*, 307–315. [[CrossRef](#)] [[PubMed](#)]
29. Jorgenson, C.K. Symbiotic ligands, hard and soft central atoms. *Inorg. Chem.* **1964**, *3*, 1201–1202. [[CrossRef](#)]
30. Pearson, R.G.; Songstad, J. Application of the principle of Hard and Soft acids and bases to Organic Chemistry. *J. Am. Chem. Soc.* **1967**, *89*, 1827–1836. [[CrossRef](#)]
31. Surpateanu, G.; Dorohoi, D.O. Determination of the group electronegativity. *An. Univ. Al. I. Cuza Sect. Ib Fizica* **1977**, *23*, 99–102.
32. Dorohoi, D.O.; Partenie, D.H.; Calugaru, A.C. Specific and universal interactions in Benzo-[f]-Quinolinium Acetyl-Benzoyl Methylid (BQABM) solutions; excited state dipole moment of BQABM. *Spectrochim. Acta A* **2019**, *213*, 184–191. [[CrossRef](#)]
33. Spartan'14 for Windows, Macintosh and Linux, Tutorial and User's Guide, January 10, 2014 Modeling. 2014. Available online: <http://downloads.wavefun.com/Spartan14Manual.pdf> (accessed on 3 June 2020).
34. Kawschi, A. On the estimation of excited state dipole moments from solvatochromic shifts of absorption and fluorescence spectra. *Z. Nat.* **2002**, *57*, 255–262.
35. Kamlet, M.J.; Abboud, J.I.; Abraham, M.; Taft, R.W. Linear solvation energy relationships 23. A comprehensive collection of the solvatochromic parameters π^* , α , β and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.* **1983**, *48*, 2877–2887. [[CrossRef](#)]
36. Nadejde, C.; Creanga, D.E.; Humelnicu, I.; Dorohoi, D.O. Study of intermolecular interactions in rifampicin ternary solutions. *J. Mol. Liq.* **2009**, *150*, 51–55. [[CrossRef](#)]
37. Morosanu, A.C.; Benchea, A.C.; Babusca, D.; Dimitriu, D.G.; Dorohoi, D.O. Quantum mechanical and solvatochromic characterization of Quercetin. *Anal. Lett.* **2017**, *50*, 2725–2739. [[CrossRef](#)]
38. Babusca, D.; Morosanu, A.C.; Dorohoi, D.O. Spectral study of specific interactions between zwitterionic compounds and protic solvents. *Spectrochim. Acta A* **2017**, *172*, 58–64. [[CrossRef](#)] [[PubMed](#)]
39. Dorohoi, D.O.; Surpateanu, G.; Gheorghies, L.V. A spectral method for determination some molecular parameters of cycloimmonium ylids. *Balk. Phys. Lett.* **1998**, *6*, 198–203.
40. Dorohoi, D.O. Excited state molecular parameters determined by spectral means. *Ukr. J. Phys.* **2018**, *63*, 701–707. [[CrossRef](#)]
41. Pantil, S.K.; Wari, M.N.; Yohannan Panicker, C.; Inamdar, S.R. Solvatochromic study of coumarin 545 in alcohols for the determination of ground and excited state dipole moments. *Int. J. Adv. Res.* **2013**, *1*, 616–626.
42. Thipperudrappa, J. Analysis of solvatochromism of a biologically active ketocyanine due using different solvent polarity scales and estimation of dipole moments. *Int. J. Life Sci. Pharma Res.* **2014**, *4*, 1–11.
43. Zakerhamidi, M.S.; Golghasemi Sorkhabi, S.H.; Shamkhali, S. Polar and low polar solvents media effect on dipole moments of some diazo-Sudan dyes. *Spectrochim. Acta A* **2014**, *127*, 340–348. [[CrossRef](#)]
44. Gahlaut, R.; Tewari, N.; Bridhkoti, J.P.; Koshi, H.C.; Pant, S. Determination of ground and excited state dipole moments of some naphthols using solvatochromic shift method. *J. Mol. Liq.* **2011**, *163*, 141–146. [[CrossRef](#)]
45. Pop, V.; Dorohoi, D.O.; Delibas, M. Considerations on the statistic model of the intermolecular interactions in ternary solutions. *An. Stiin. Univ. Al. I. Cuza Iasi* **1987**, *33*, 78–86.

46. Dorohoi, D.O.; Pop, V. Spectral shifts of the electronic absorption spectra of some cycloimmonium ylids in ternary solutions. *An. Stiint. Univ. Al. I. Cuza Iasi Ib Fizica* **1987**, *33*, 78–85.
47. Puica-Melniciuc, N.; Avadanei, M.I.; Caprosu, M.; Dorohoi, D.O. Interaction energy in pairs of phthalazinium-dibenzoyl methylid (PDBM)–protic solvent molecules estimated in the limits of ternary solution model. *Spectrochim. Acta A* **2012**, *96*, 271–277.
48. Dorohoi, D.O.; Avadanei, M.; Postolache, M. Characterization of the solvation spheres of some dipolar spectrally active molecules in binary solvents. *Optoelectron. Adv. Mater.* **2008**, *2*, 51–55.
49. Avadanei, M.; Dorohoi, D.O. Interaction energy in pairs of pyridazinium ylid-solvent molecules estimated by spectral means within the cell ternary solution model. *Ukr. J. Phys.* **2012**, *57*, 118–122.
50. Sasirekha, V.; Vanelle, P.; Terme, T.; Ramakrishnan, V. Solvatochromism and preferential solvation of 1, 4-dihydroxy-2, 3-dimethyl-9, 10-anthraquinone by UV-vis absorption and laser-induced fluorescence measurements. *Spectrochim. Acta A* **2008**, *71*, 766–772. [[CrossRef](#)] [[PubMed](#)]
51. Buhvestov, U.; Rived, F.; Ràfols, C.; Bosch, E.; Rosés, M. Solute-solvent and solvent-solvent interactions in binary solvent mixtures. Part 7. Comparison of the enhancement of the water structure in alcohol-water mixtures measured by solvatochromic indicators. *J. Phys. Org. Chem.* **1998**, *11*, 185–192. [[CrossRef](#)]
52. Rosés, M.; Buhvestov, U.; Ràfols, C.; Rived, F.; Bosch, E. Solute-solvent and solvent-solvent interactions in binary solvent mixtures. Part.6. A quantitative measurement of the enhancement of water structure in 2-methylpropan-2-ol-water and propan-2-ol-water mixtures by solvatochromic indicators. *J. Chem. Soc. Perkin Trans.* **1997**, *2*, 1341–1348. [[CrossRef](#)]
53. Dulcescu, M.M.; Stan, C.; Dorohoi, D.O. Spectral investigations of the influence of the hydroxyl solvents on the intermolecular interactions in some pyridinium ylid ternary solution. *Rev. Chim. Buchar.* **2010**, *61*, 1219–1222.
54. Dulcescu, M.M.; Stan, C.; Dorohoi, D.O. Spectral study of intermolecular interactions in water-ethanol solutions of some carbanion di-substituted pyridinium ylids. *Rev. Roum. Chim.* **2010**, *55*, 403–408.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).