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# Theoretical study of electronic absorptions in aminopyridines – TCNE CT complexes by quantum chemical methods, including solvent

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**Abstract** The geometric and electronic structure of donor-acceptor complexes of TCNE with aniline, o-, m- and p-aminopyridines and pyridine has been studied in gas phase and in solution using CC2, TDDFT and CIS methods. Concerning interaction energy between particular donor and TCNE acceptor it is fairly described by both CC2 (MP2) and DFT-D approaches. Transition energies in gas phase calculated by CC2 approach are in good agreement with available experimental data for aniline. TDDFT calculations with LC-BLYP functional (with standard value of range separation factor $\mu=0.47$) gives transition energies too high although not as high as CIS. The red solvent shifts, calculated by PCM model with CIS method are qualitative correct, but error in the range of 0.1-0.2 eV should be expected.

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## Introduction

Aminopyridines are bioactive *N*-heterocyclic tertiary amines that increase the strength of the nerve signal. Due to their ability to facilitate nerve transmission, aminopyridines have been applied to reverse anesthesia and muscle relaxation. In addition, they have been proposed as drugs for the treatment of multiple sclerosis, myasthenia gravis, spinal cord injuries, botulism and Alzheimer's disease [1].

2-aminopyridine (2AMP) is also a structural mimic of the Watson–Crick hydrogen binding site of adenine, offering both an N–H donor and an aromatic N acceptor group [2–6]. For this reason, 2AMP and its self-dimer $(2AMP)_2$ have been widely employed as models for doubly hydrogen-bonded DNA base pairs in the gas phase [7–13].

Charge-transfer (CT) interactions are among key interactions, used for preparation of foldamers, specific chemical contribution to study of folding properties of biological macromolecules, e.g. proteins [14]. The study of CT-interactions between aromatic electron acceptors and various electron donors containing nitrogen, oxygen, or sulfur atoms have attracted increased research interest over the last years. This is because of the important roles these interactions play in biological systems; beside that CT-complexes act as intermediates in a wide variety of reactions involving nucleophiles and electron acceptor molecules [15].

Tetracyanoethylene (TCNE) molecule is one of the most versatile organic compounds as it is used in many different reactions, due to its very low-lying $\pi^*$ orbital. After the pioneering work on electron transfer phenomena in

TCNE – hexamethylbenzene CT complex [16] by Mulliken and others, it has been revealed that the theoretical justifications on energies and types of CT transitions play a crucial role in interpreting the UV–VIS spectral behavior of such molecule. Recently, Miller et al. extensively studied the characteristic geometries and vibrational absorptions of various numerous structural aspects of TCNE [17].

Till date, there are a few reports on theoretical prediction on the ground and excited state complexation phenomena between TCNE and some other aromatic amines molecule having electron donation capability. Liao et al. [18] studied experimentally and theoretically (at the BHandHLYP/6-31G* level) the formation of CT complexes of several aromatic amines and nitrogen heterocycles with TCNE and chloranil. DFT calculations of aniline-TCNE complex have been carried out including solvent effect by PCM approach in order to understand the energetics and origin of the CT spectra. By calculating electron excitation energies ($E_{exc}$) and D-A binding energies ($E_{bind}$), the most probable geometric structures of the complexes that are responsible for the absorption bands were determined. The consideration has been limited only for two similar conformations, which have mutually perpendicular orientation of TCNE molecule, forming parallel stacked structures. The intermolecular distance between parallel D and A planes is calculated to be 3.16 and 3.23 A. Experimental spectrum of this complex shows a broad, intense band with a peak at 2.14 eV, which was attributed to HOMO-LUMO transition [18]. Frey et al. [19] reported on earlier spectral measurement of arylamine-TCNE complexes in dichloromethane two strong bands at ca. 2.1 and 3.2 eV. The calculated BHandHLYP/6-31G* HOMO-LUMO and LUMO-1 transitions by the Liao et al. [18] are 1.90 and 3.02 eV.

Manna et al. [20] also studied theoretically the charge-transfer complex of aniline-TCNE in gas phase on the HF/3-21G* and B3LYP/6-31G* levels. In calculated geometrical conformation of the complex, the amine group was located under C atom of TCNE C = C bond, similarly as it is at shifted conformation in our study (see later). The calculated B3LYP/6-31G* HOMO-LUMO transitions energies at this conformation is 2.36 and 4.24 eV, with oscillator strengths close to 0.

Mostafa et al. [21] experimentally studied the interactions of the 2AMP and 3-aminopyridine (3AMP) with TCNE. Electronic and infrared spectra of the formed CT complexes in acetonitrile and chloroform were measured. The formed 2AMP-TCNE and 3AMP-TCNE complexes showed strong absorptions centered on 384 and 344 nm for 2AMP-TCNE and 3AMP-TCNE respectively. The spectrophotometric data were used to calculate some physico-chemical characteristics. The formation constant $K$ of 2AMP-TCNE and 3AMP-TCNE were determined to be 0.095 $10^3$ resp. 0.138 $10^3$ dm$^3$.mol$^{-1}$ (in CHCl$_3$) and molar extinction coefficient $10^{-2}$ -$10^{-3}$ dm$^3$ mol$^{-1}$ cm$^{-1}$. The energy of CT transitions in these complexes were experimentally determined at 3.24 and 3.62 eV, resp. Here it should be noted that such K values for TCNE complexes with aromatics seem to be by 2–3 orders too large and determined molar extinction 4–5 orders too low. More than that, energies of found absorptions are higher than experimentally determined energies [18, 19] of first two absorptions of TCNE – aniline complex (2.14 and 3.2 eV).

However, when aminopyridines are forming CT complexes with TCNE, except for pure π complex also chemical reactions and formation of other complexes is possible. For example in papers by Bruni et al. [22] and Midletton et al. [23] it was found, that in the presence of water molecules the pentacyanopropenyl anion salt with hydropyridyl cation is formed, so that except for absorption spectrum of pure π – complex also the spectrum of pentacyanopropenyl anion is observed with very intensive molar extinction equal ca. 22 000 units [22]. This fact certainly should be taken into account when studying complexation of TCNE with aminopyridines in various solvents.

To formation of CT complexes between TCNE and some hydrocarbon aromatic donors we have devoted extensive research efforts [24–27]. We have thoroughly studied geometries, thermodynamics, and electronic UV–VIS and IR spectra of methyl substituted benzenes with TCNE. From this experience we might conclude that reliable theoretical data can be obtained using quantum-chemical methods which accurately consider intermolecular electron correlation, i.e., dispersion part of interaction energy between respective π donor and π acceptor. Among these the nonempirical methods at least on MP2 or CC2 levels are necessary to be applied to large π [20] complexes of CT type. As to DFT approaches the reasonable results were obtained from dispersion corrected DFT-D [28]. For adequate understanding of electronic absorption and emission transitions the CC2 method appeared to be feasible and precise with almost benchmark quality. PCM model in CIS or LC- corrected LC-BLYP [29] methods is very useful as semi-quantitatively accounting for importance of solvent effect both on the ground state and especially excited state properties.

In the present article we aimed at application of nonempirical, DFT and PCM approaches to account for UV–VIS spectra of CT complexes formed between a class of aminopyridine donors and TCNE acceptor. Very recently [30] we have studied electronic absorption and emission spectra in similar CT complexes – methylated benzenes (nMB) with TCNE. There was used very similar methodology. It was found that for gas phase the RI-CC2/aug-cc-pVTZ absorption transition energies are closed to experiment, but still by 0.1 -0.15 eV lower than experimental values. Further, in the studied complexes polar solvents shift absorption transitions bathochromicaly (red shift) according to configuration interaction with single excitations and PCM

inclusion of solvent (CIS(PCM)) calculations by average value ca. 0.05-0.1 eV while experimental values are systematically much larger and equal to ca. 0.2 eV. We used this experience in present study of similar CT systems, i.e., TCNE – aminopyridines complexes.

## Methodology

According to our previous experience with EDA complexes all systems have been optimized at the B97-D [30] level of theory using the 6-311 + G(2d,2p) [31, 32] basis set. In order to ensure local minima character of obtained stationary points we carried out frequency calculations at this level. BSSE correction was in this case not taken into account explicitly, since it is assumed to be quite small for basis set of this size and it is effectively absorbed in the parametrization process of this approach [28, 30]. For comparison, energy minima and (BSSE corrected [33]) interaction energies were also calculated at RI-MP2/def2-TZVPP level. For aniline and o- aminopyridine we make also BSSE corrected RI-MP2/def2-TZVP optimization. As expected, all intersystem distances were systematically larger by 0.05A and all interaction energies (compared to *a posteriori* BSSE corrected RI-MP2/def2-TZVP values) were different by less than 1 kJ mol$^{-1}$. For these reasons we do not continue this strategy for remaining molecules. In all cases several energetically close local minima were found. Using the optimized structures excitation energies of four lowest excited states were computed by means of configuration interaction singles (CIS) [34], approximate coupled cluster including single and double excitations [35], (RI-CC2 with resolution of identity to speed up the calculation [36]) and time-dependent DFT (TD-DFT). In these excitation energy calculations standard Dunning´s correlation consistent basis set aug-cc-pvDZ [37, 38] was used. In the case of aniline also larger aug-cc-pvTZ basis was used to confirm our findings from previous works [26, 27] that the size of chosen basis set is not limiting factor in excitation energy calculations. Indeed, difference between excitation energies in these two bases was less than 0.05 eV. For the RI approach, the appropriate auxiliary basis sets were utilized [39].

It is well-known that standard local density approximation (LDA) and generalized gradient approximation (GGA) DFT methods tend to perform poorly in a number of important applications. In the context of the present study let us mention especially the poor description of charge transfer excitations [40, 41]. These failures have been thoroughly analyzed and they were attributed to an incorrect asymptotic behavior of the exchange-correlation part of the DFT functional [42]. A promising way to correct this deficiency has been to keep DFT-like short-range exchange while switch to the HF exchange smoothly at longer distances. There are

several implementations of this basic idea. One can either employ gradient or local functionals to obtain LR corrected functionals such as LC-BLYP [29], or to use the well-known hybrid B3LYP functional in the CAM-B3LYP hybrid form [43]. In this study we used LC-BLYP [44] functional with aug-cc-pvDZ basis set for TD calculation of transition energies both in vacuum and in solvent. In these calculations GAUSSIAN09 [45] standard value of range-separation parameter μ=0.47 was used.

Polarizable continuum model (PCM) [46] in its Gaussian09 [45] implementation has been used to treat solvent effects on excitation energies, at both CIS and LC-BLYP levels. Nonequilibrium solvation model was used in the case of absorption transitions.

Geometry optimizations and vibrational frequency calculations at DFT-D and CIS and LC-BLYP TD-DFT excitation energies were calculated using Gaussian09 [45] package both *in vacuo* and in solvent. All RI-CC2, and RI-MP2 calculations were done in Turbomole Ver. 5–10 [47].

## Results and discussion

Since there are more geometries of particular complex with own energy minima differing from each other by several tenths of kJ mol$^{-1}$, we are aware that for more precise comparison of calculated and corresponding experimental properties one has to take into account Boltzmann populations of individual conformational minima in the respective electronic state. However, since we have only a few experimental data on aniline – TCNE complex we did not realize such a detail study and we have chosen to discuss only properties in one or two geometries with the lowest energies.

Geometry and interaction energy in the complexes

Table 1 contains calculated data on geometry of the most stable parallel stacked structure (minima) of the complexes of aniline, orto-, meta-, para- aminopyridnes and pyridine with TCNE. In the Table 1 the intersystem distances R and interaction energies by both CC2 and DFT-B97D methods are included. The most stable geometries for all complexes are drawn in Scheme 1. However, except for this structures there are others geometries with minimum of energy which are only by tenths or a few kJ mol$^{-1}$ higher and we did not include them in the Table 1. All structures can be roughly divided into two classes.

First class forms the structures where TCNE is above benzene ring and they are similar to those found for complexes of methylbenzenes with TCNE [26] these are like, e.g., structures – AN2, AN_Cs, P_Cs and some others (see Scheme 1). The second class contains structures in which TCNE molecule, especially its C atoms of C = C moiety, are located above N atom of NH$_2$ group and we designated

**Table 1** Calculated interaction energy $E_{int}$ (kJ mol$^{-1}$), enthalpy $\Delta H_{int}$ (kJ mol$^{-1}$), Gibbs energy $\Delta G_{int}$ (kJ mol$^{-1}$) and correction for vibration zero point energy $\Delta ZPE$ (kJ mol$^{-1}$) of the complexes between TCNE and respective donor molecule, intersystem distance R (A) in the complex, calculated and experimental IPs (eV) of donors

| donor molecule (structure of complex – Scheme 1) | B97D 6-311+G(2d,2p) | | | | | RI-CC2[a] aug-cc-pvDZ | RI-MP2 def2-TZVPP | | OVGF IP[b] (exp) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | R | $E_{int}$ | $\Delta ZPE$ | $\Delta H_{int}$[c] | $\Delta G_{int}$[c] | $E_{int}$ | R | $E_{int}$ | [eV] | |
| Aniline (AN2) | 3.05 | −67.4 | 5.3 | −60.9 | −15.0 | −66.8 | 2.84[d] | −65.0[d] | 8.03 | (8.05) |
| Aniline (AN_Cs) | 3.05 | −66.0 | 4.7 | −62.2 | −8.2 | −66.9 | 2.84 | −65.0 | | |
| o-AMP, (M1 ) | 3.08 | −55.2 | 4.2 | −49.3 | −4.7 | −55.6 | 2.91 | −53.3 | 8.378 | (8.34) |
| o-AMP, ( o-Sh1) | 3.02 | −53.7 | 3.9 | −47.9 | −4.4 | −58.6 | 2.88 | −56.7 | | |
| m-AMP, (T1 ) | 3.08 | −57.4 | 4.2 | −51.3 | −7.6 | −58.4 | 2.90 | −56.5 | 8.397 | (8.44) |
| m-AMP, (m-Sh1) | 2.87 | −56.4 | 3.4 | −50.5 | −4.9 | −58.6 | 2.74 | −56.6 | | |
| p-AMP (P1 ) | 3.11 | −51.9 | 3.7 | −46.1 | −3.5 | −57.0 | 2.94[e] | −55.5[e] | 8.631 | (8.76) |
| p-AMP (P_Cs) | 3.07 | −50.8 | 3.7 | −47.4 | 3.9 | −57.8 | 2.94 | −55.5 | | |
| Pyridine(Par_C1) | 3.18 | −34.3 | 2.9 | −28.6 | 6.1 | −41.8 | 3.04 | −41.0 | 9.669 | (9.66) |
| Pyridine(Perp_Cs) | 2.81 | −41.8 | 2.9 | −36.0 | −3.3 | −43.9 | 2.69 | −41.0 | | |

[a] in B97D/6-311 + G(2d,2p) geometry

[b] calculated at OVGF/aug-cc-pvQZ basis, exp. values from ref.[48, 49]

[c] at standard conditions

[d] collapses at this level to AN_Cs structure

[e] collapses to P_Cs structure

Intersystem distance is defined as a distance from geometrical center of nonhydrogen atoms of aromatic ring from centre of C = C bond in TCNE, For Sh1 geometries, it is defined as a distance from C atom of C = C bond in TCNE to N atom of NH$_2$ group

them as Sh (i.e., shifted) structures like o-Sh1, m-Sh1. In the case of pyridine-TCNE complex except for parallel stacked structure Par_C1 ($\pi$-$\pi$ complex) also close in energy perpendicular structure exists in which TCNE plane is directed towards lone electron pair in pyridine (this complex is usually called n-$\pi$ complex), i.e., the structure Perp_Cs.

Though there is not clear linear dependence between interaction energy and intersystem distance R (Fig. 1), general trend can be observed: with larger intersystem distances the interaction energy is higher. Also a quite good linear dependence between B-97D and CC2 or MP2 values was found. MP2 values are essentially the same as CC2 values despite the fact that different basis sets are used (aug-cc-pvDZ for CC2 and def2-TZVPP for MP2) and the lathers are calculated in MP2 optimized geometries having shorter distances by about 0.2 A (see Table 1). As to difference between B-97D interaction energies and MP2 values, it illustrates general good performance of DFT-D for intermolecular interactions, although it is seen that the MP2 energies, especially for smaller values, are slightly lower than that of B97-D (see Table 1). What should be mentioned in this context is discrepancy in fine angular dependence of interaction energy for parallel rotation of TCNE above the donor aromatic ring. Here we observed in some cases that DFT-D potential curve has more pronounced angular dependency and this method tends to prefer unsymmetrical orientations contrary to MP2 (see Table 1, aniline AN_Cs and p-AMP, P_Cs as examples).

The reasons for changes in the interaction energies between different complexes should be looked for in the different degree of $\pi$-donor ability of considered donor. This property is directly connected with first ionization potential of the donors. OVGF/aug-cc-pvQZ calculated results are included in the Table 1. Data of MP2 interaction energy and experimental IPs [48, 49] plotted in Fig. 2, really indicate a good linear dependence with the slope 13.7 kJ mol$^{-1}$ eV$^{-1}$=0.14 thus showing that about 14 % of the change in IP is projected to intermolecular interaction energy. More than that in all aminopyridines the HOMO orbitals (either in aniline or in benzene itself) is strongly stabilized by electronegative N-atom at aza substitution and thus the respective IP value is increased. It is also interesting that p-aminopyridine has significantly higher IP than both o- and m- derivatives which is caused by higher stabilization of its HOMO due to mutual geometric and electronic position of N atom of aza group relatively to NH$_2$ group. Here we notice that Fig. 2 also contains dependence between excitation energy and IP of studied aminopyridines. This dependence is discussed in respective paragraph.

Table 1 also contains the calculated results on enthalpies and Gibbs energies of formation of studied $\pi$-complexes in a gas phase. However, we underline that all these data are calculated in approximation of harmonic oscillator (which is

**Scheme 1** Geometries of discussed minima, meaning of their abbreviation is given in the text
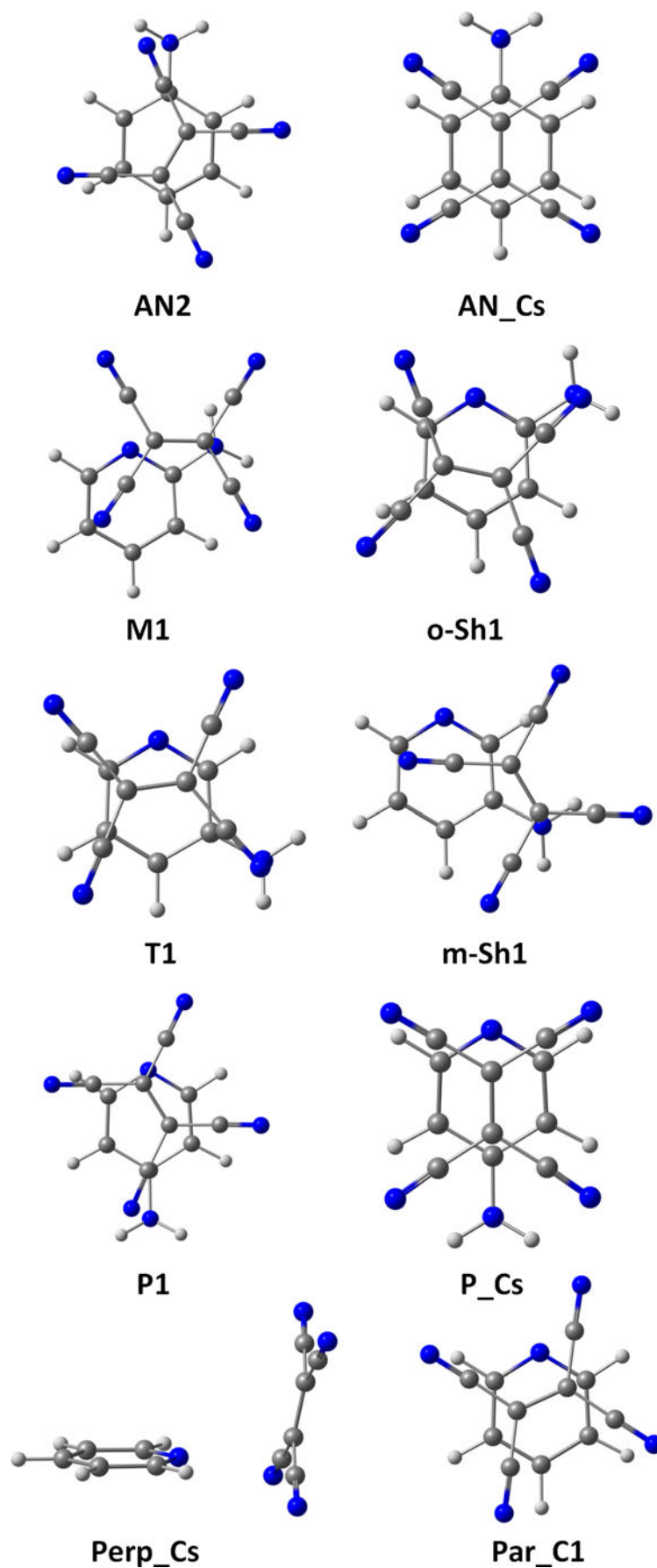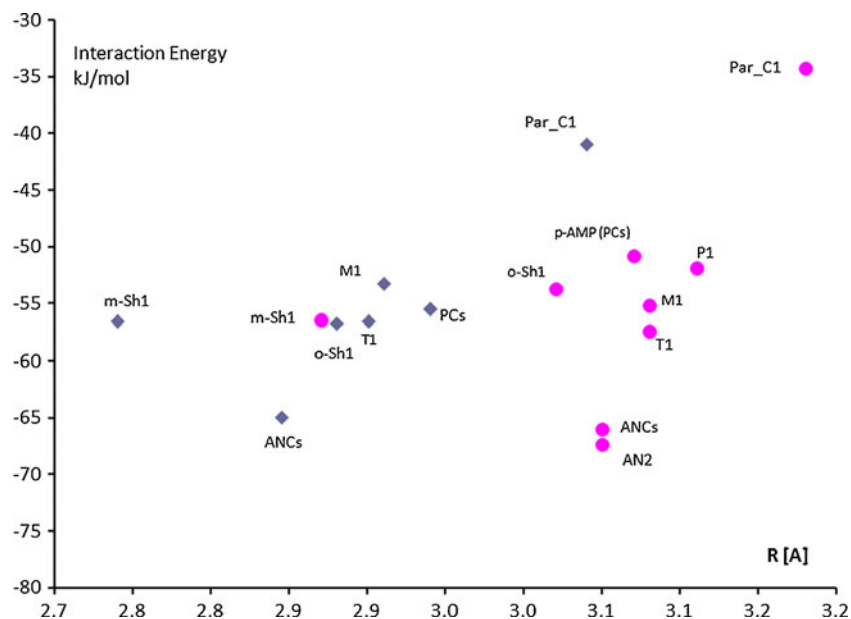


AN2

AN_Cs

M1

o-Sh1

T1

m-Sh1

P1

P_Cs

Perp_Cs

Par_C1

**Fig. 1** The plot of interaction energy vs. intersystem distance R between TCNE and respective donors. (for geometries see Scheme 1) for MP2 (◇) and B97-D (•)



poorly fulfilled for weak vibrations which, in their turn, decidedly contribute to entropy of complex formation) and rigid rotator; and solvent effects are not taken into account at all, so that calculated data, esp. those on Gibbs energy, should be taken with a great caution and used only for a rough orientation. More than that, in such close lying multi-minima systems the entropy is influenced by additional phenomena as are, e.g., hindered rotation, couplings between vibration and rotation motions and so on.

We have observed that there is quite a scattered dependence between distance R optimized by DFT (B97-D) method and those obtained by MP2 approach, while mutual correlation between B97-D and MP2 energies is in good approximation linear. Still at weaker complexes like p-AMP-TCNE and especially, pyridine-TCNE the

B97-D interaction energies are too small (in absolute value). That is, particularly, why we are testing a new version of DFT-D parameterization [50]. We also mention that comparison between calculated B97-D vs. MP2 interaction energy reveals a difference in dependences on the angle of parallel rotation in aniline-TCNE complex. From MP2 calculations of interaction energies between TCNE and nMB benzenes, for example with benzene molecule (IP=9.24 eV) and hexamethyl-benzene (IP= 7.85 eV) one can see that these complexes have similar values of interaction energy as complexes of TCNE with pyridine (IP=9.25 eV) and aniline (IP=7.72 eV). Such a situation is met because of very similar value of first IPs of the donors and similar stacked parallel structures of their complexes with TCNE.

**Fig. 2** Dependences of MP2/ def2-TZVPP interaction energy [kJ mol$^{-1}$] and RI-CC2 /aug-cc-pVDZ calculated first CT transition energy of studied complexes on experimental first IP [eV] of respective aminopyridines. Open circles (o) and crosses (+) stand for two selected conformation of complex, rhomboids (◊) designate transition energies of first CT absorption
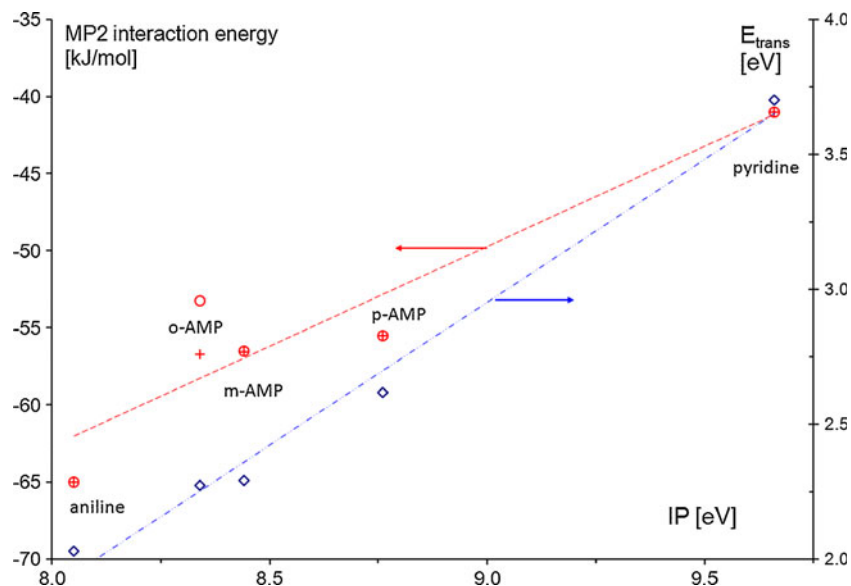
We can also emphasize the above mentioned fact that pyridine can form EDA complex with TCNE not only in the stacked but as well as in perpendicular geometry. Essentially both structures reveal similar values of interaction energy (Table 1). However we believe that σ complex in n-π geometry might be more stable because of its anticipated less ordered structure having larger entropy than parallel stacked one. More than that, polar solvents should stabilize n-π complex to higher degree than π-π complex.

Effect of geometry optimization on CC2 excitation energies

During study of excitation transitions in complexes of aniline and aminopyridines with TCNE treated by CC2 method we have found that CC2 energies corrected by PCM solvent effect still are by ca. 0.15 eV lower than experimental excitation energy measured for aniline-TCNE complex in acetonitrile [18]. This small but significant discrepancy we explain by geometry of the complex. After gas phase geometry optimization by MP2/def2-TZVPP method (with BSSE correction), it was found, that intermolecular distance is shorter (3.0 A in MP2 and 3.1 A in DFT-D). Calculated CC2 first excitation energy (PCM corrected for solvent) for MP2 geometry is almost the same as experimental value. We regard correction of geometry optimization by MP2 calculation as important, leading to better agreement between calculated and experimental excitation energy, at least for complexes studied in this paper.

Electronic absorption transitions

The data on CC2, CIS and LC-BLYP calculations are given in Table 2. As we have indicated in the Introduction due to high mutual chemical reactivity between TCNE and aminopyridines only electronic absorption spectra in aniline-TCNE complex is reliable experimentally recorded [18, 19]. The first absorption band has $\lambda_{max}$ at 576.7 nm, which correspond to 2.14 eV, and second band is located at 3.3 eV. Because of a

good accuracy of CC2 absorption and emission transitions energies in our above mentioned study of stacked complexes of TCNE with methylated benzenes, we use this reliable method to calculate electronic transitions also in complexes with aminopyridines as well. The data in Table 2 show a picture which is common also to CT complexes of methylbenzenes complexes with TCNE: CC2 gives the values of transition energies which are close to experiment, while CIS results are more than 1 eV too high and the results of popular TD-DFT LC-BLYP (with factor μ=0.47) lie somewhere between them. Though, CC2 value for aniline – TCNE complex (1.997 eV with optimized DFT-D geometry) is close to experiment, however, experimental value is little larger (2.14 eV in acetonitrile). We also optimized geometry by MP2 and received intermolecular distance equal to 2.85 A vs. 3.05 A obtained by B97-D method. Indeed, because of closer spatial proximity of aniline molecule to TCNE the CC2 transition energy is closer to experiment (2.205 eV, Table 2). The rest of the difference to experiment, i.e., 2.205 - 2.14=0.054 eV is probably due to red shift caused by solvent in which spectrum was measured (see PCM results later). Though this red shift is in the correct direction, according PCM calculation at changing gas phase to chloroform the shift is larger being ca. 0.15 to 0.2 eV. We conclude that at CC2 level with PCM correction for solvent effect can reach accuracy of about ±0.1-0.2 eV for these CT complexes of amino and/or aza- benzene donors with TCNE.

As to dependence of the energy of first transition in o-, m-, p-aminopyridines and pyridine complexes this can be easily understood. The increase in transition energy is directly connected with the energy of HOMO orbital in respective donor - equal to ionization potential according to Koopmans's theorem. No wonder that more electronegative aza-substitution stabilizes respective HOMO in original aniline molecule. As described before the HOMO in p-derivative is the most stabilized. Thus HOMO orbitals in o- and m- derivatives are less stabilized than that in p- aminopyridine due to both the structure of anilines' HOMO (with much larger value of respective HOMO expansion coefficient in p- position

**Table 2** RI-CC2, CIS and LC-BLYP absorption transitions energies $E_{trans}$ (eV) and oscillator strengths $f$ for complexes of TCNE with respective donors. Basis set used is aug-cc-pVDZ. (For designation of complex structures see Scheme 1)

| Donor molecule (complex structure) | RI-CC2 (B97-D geometry) | | RI-CC2 (MP2geometry) | | CIS (B97-D geometry) | | CIS (MP2geometry) | | LC-BLYP (B97-D geometry) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ |
| Aniline (AN_Cs) | 1.997 | 0.105 | 2.205 | 0.125 | 3.333 | 0.146 | 3.498 | 0.187 | 2.712 | 0.100 |
| o-AMP, (M1 ) | 2.273 | 0.123 | 2.456 | 0.127 | 3.663 | 0.153 | 3.814 | 0.172 | 3.026 | 0.112 |
| m-AMP, (T1, ) | 2.292 | 0.125 | 2.490 | 0.146 | 3.604 | 0.157 | 3.764 | 0.205 | 3.023 | 0.116 |
| p-AMP (P_Cs ) | 2.617 | 0.060 | 2.680 | 0.068 | 4.223 | 0.077 | 4.261 | 0.103 | 3.495 | 0.075 |
| Pyridine (Par_C1) | 3.700[a] | 0.052 | 3.706[a] | 0.061 | 4.651 | 0.077 | 4.625 | 0.091 | 4.175 | 0.054 |
| Pyridine (Perp_Cs) | 3.674 | 0.190 | 3.733 | 0.204 | 5.000 | 0.592 | 5.000 | 0.591 | 4.434 | 0.374 |

[a] Second transition, first (forbidden) transition is of n-π* type

relatively to o- and m- derivatives) as well as due to the longest distance between N atoms of -NH$_2$ and aza- group in p- derivative. Electronic $\pi-\pi^*$ transition in pyridine – TCNE complex, is essentially that in benzene – TCNE complex, however, being at higher energy since IP of pyridine is somewhat larger (9.66 eV) than that of benzene itself (9.25 eV). The difference is certainly caused by the presence of electronegative N atom in pyridine, which stabilizes also $\pi$- HOMO of benzene, though 2p$_z$ AO of N is not involved in this $\pi$ - HOMO. We also notice (Table 2) that n-$\pi^*$(TCNE) transition energy is even smaller (3.67 eV) as just above mentioned $\pi-\pi^*$ transition, though n - orbital is the third occupied (i.e., HOMO-2) with much smaller energy ($-10.89$ eV) than respective $\pi$ – HOMO orbital ($-9.7$ eV). The explanation of this is very similar to that found in the case of both $\pi-\pi^*$ and n-$\pi^*$ transition energies in pyridine itself: Due to a rather localized nature of n- orbital the corresponding energy of n-$\pi^*$ transition (3.67 eV) is bathochromicaly shifted even to the energy of first $\pi-\pi^*$ transition (3.70 eV) because of much larger attractive interaction energy between localized positive hole on n-orbital and negative charge on $\pi^*$ LUMO at the excitation (i.e., because of $C$ term in the mentioned simplified equation connecting $h\nu$ with $IP$ – see below). We mention here also the fact, that the distance N…TCNE in perpendicular geometry (2.8 A) is shorter than in parallel $\pi$-complex (3.1 A) and n-orbital is significantly localized at N atom being directed face-to-face with $\pi^*$-LUMO located on TCNE moiety.

Oscillator strength

We touch also oscillator strengths values for the first CT transitions in the studied complexes (Table 2). From the data one can conclude that TCNE complexes with aniline and o- and m- aminopyridines are the most intensive with $f$ values higher than 0.1 a.u. (CC2 calculations), while complexes with p-derivative and pyridine itself have much smaller intensity with $f$=0.06 and 0.05 resp. This is in rough accord with the values of ionization potentials: the higher IP, the less intensive the transition. Though calculated optimized geometries in the same complex are very similar in energy, some differences between oscillator strengths for the first transition have been found. We also note that first electronic transition in pyridine-TCNE complex with perpendicular geometry (Perp_Cs) ($\sigma$-complex of Cs symmetry) is not forbidden by the symmetry and is much more intensive ($f$=0.156) that the first allowed $\pi$-$\pi^*$ transition ($f$=0.06) in parallel stacked geometry of the complex. This fact is caused by a relatively large transition overlap density (n $x$ $\pi^*$) due to mutual perpendicular geometry of the constituents. As to the second CT transition in aniline – TCNE complex, and analogously for this transitions in aminopyridines complexes it was found that CC2 transition energy lies at 3.35 eV with $f$=0.03 This transition energy is relatively close to experiment (3.2 eV in dichloromethane) [19]. While

CC2 transition energies for the first and second transitions correspond closely to experiment in the case of aniline complex, however no – even qualitative – agreement was found with recent experimental study both of o- and m- AMP – TCNE spectra by [21]. We suppose that these experimental spectra do not correspond to CT transitions of the postulated $\pi$- complexes and experimental spectra are probably due to some intermediates or products of real chemical reactions taking place between TCNE and above mentioned aminopyridines. This is also supported by rather unrealistic values of their experimentally found equilibrium constants of complex formation (ca. 10$^3$ dm$^3$.mol$^{-1}$) and found molar extinction coefficients (ca. 10$^{-2}$ dm$^3$.mol$^{-1}$.cm$^{-1}$) while CT complexes between TCNE and many aromatic donors have equilibrium constants ranging from 10$^{-1}$ to 10$^1$ dm$^3$.mol$^{-1}$ and molar extinction coefficients from 10$^2$ to 10$^3$ dm$^3$.mol$^{-1}$.cm$^{-1}$ [19].

Dependence between transition energy and IP

Figure 4 indicates a good linear dependence between these two quantities for $\pi-\pi^*$ transitions in the respective complexes. This follows from the simplified equation for transition in CT complexes:

$$h\nu = IP(D) - EA(TCNE) + C \qquad (1)$$

where *IP(D)* stands for ionization potential of respective donor molecule, *EA* is electron affinity of TCNE and *C* contains different terms originating from quantum chemical calculations where the important one is the term expressing coulombic attraction between amount of electron transferred to TCNE and respective positive hole on donor molecule. Since this term and thus $C$ value is changing in donor-TCNE series of complexes probably insignificantly, linear dependence between $h\nu$ and $IP(D)$ is expected. Linear dependence in Fig. 2 has the slope 1.06 and is expressed by equation: $h\nu = 1.06IP(D) - 3.2eV - 3.37eV$, where 3.2 eV is experimental value of EA of TCNE and $-3.37$ eV is connected with the mentioned Coulombic attraction roughly equal to $q_{CT}^2/4\pi\varepsilon_0 R$ with $q_{CT}$ being transferred charge in particular excited state of the complex.

Analogous linear dependence was found also for second CT transition in the studied systems. However, some care should be taken to compare the states with similar electron distribution of particular excited state in complexes with different donors. For example, do not mix CT $\pi$-$\pi^*$ with n-$\pi^*$ transitions. Similar linear dependences have also been found for nMB – TCNE complexes [28], however, with the slope 0.73. We did not expect the same slopes of linear dependences also for so different donors as are studied here aminopyridines. It seems that the decisive role is the presence of aromatic donors in stacked $\pi$-complexes with the same acceptor.

## Solvent effect on absorption excitations

Table 3 contains data on PCM(CIS) calculations of solvent effect for different solvents both in relative permitivity ($\varepsilon_r$) and in refractive index n. One can find red shift in the energy of the first $\pi$-$\pi$* charge transfer excitations for all complexes. This is in accord with the expectation that due to almost complete electron transfer (see Table 4) in the excited $\pi$–$\pi$* state, this state is significantly more stabilized than the ground state (in polar solvent). The solvent shift is thus dependent on polarity of the solvent. Even for modestly polar solvents such as $CCl_4$ and cyclohexane red shift reaches value 0.15 – 0.17 eV. The dependences of red shift values on argument $((\varepsilon_r-1)/(\varepsilon_r+2))-((n^2-1)/(n^2+2))$ – (which contains both "slow" and "fast" polarizations of the solvent) for all studied aminopyridines complexes have almost the same character. When changing gas phase for even slightly polar solvent as $CCl_4$ and cyclohexane the red shifts reach maximum value "very soon". When going to even very polar solvents – it stays constant. (Figure 3 for AN_Cs minimum of aniline on the CIS (PCM) model). Thus, in the non-equilibrium model, excited state feels only change of reaction field from electron polarization of solvents, represented by $n^2$ term. For all common solvents, its value is changing only in small interval, ca. from 1.8 (acetonitrile) to 2.2 ($CCl_4$). This is why solvent shifts are relatively insensitive to polarity. On the other hand, for processes modeled by equilibrium model (like transferred charges - see below- or also red shift values for studied electronic transitions with solvent equilibrated excited states) good correlation is expected with polarity functions, depending on static $\varepsilon_r$ value (like simplest relation $(1- \varepsilon_r^{-1})$ or $(\varepsilon_r-1)/(2\varepsilon_r+1)$ ).

As to values of electron charges transferred from particular donor to TCNE the situation is as follows: the stronger donor (smaller IP) the larger respective charge transfer in the ground state. The reverse is valid for excited states (Table 4). As to dependences between electron transferred charges and dielectric function $(\varepsilon_r-1)/(\varepsilon_r+2)$ it was found to be linear both in excited and ground states (as example is aniline – TCNE complex in AN1 geometry, see Fig. 4). Yet, the slope for excited state is almost 11 times greater than that for ground state. Both these linear dependences can be easily

**Table 3** Influence of solvent on the absorption transition energy $E_{trans}$ (eV) and oscillator strength $f$ calculated by CIS and LC-BLYP methods within PCM solvent model. Basis set is aug-cc-pVDZ

| Donor molecule (complex structure) | Solvent | RI-CC2 | | CIS | | LC-BLYP | |
|---|---|---|---|---|---|---|---|
| | | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ | $E_{trans}$ | $f$ |
| Aniline (AN_Cs) | gas phase | 1.997 | 0.105 | 3.333 | 0.146 | 2.712 | 0.100 |
| | cyclohexane | | | 3.156 | 0.190 | | |
| | chloroform | | | 3.122 | 0.195 | 2.565 | 0.127 |
| | dichlormethane | | | 3.123 | 0.194 | | |
| | acetonitrile | | | 3.143 | 0.189 | 2.569 | 0.124 |
| o-AMP (M1 ) | gas phase | 2.273 | 0.123 | 3.663 | 0.153 | 3.026 | 0.112 |
| | cyclohexane | | | 3.5070 | 0.200 | | |
| | chloroform | | | 3.486 | 0.204 | 2.911 | 0.140 |
| | dichlormethane | | | 3.492 | 0.203 | | |
| | acetonitrile | | | 3.514 | 0.197 | 2.928 | 0.247 |
| m-AMP (T1 ) | gas phase | 2.292 | 0.125 | 3.604 | 0.157 | 3.023 | 0.116 |
| | cyclohexane | | | 3.429 | 0.207 | | |
| | chloroform | | | 3.392 | 0.211 | 2.870 | 0.144 |
| | dichlormethane | | | 3.390 | 0.209 | | |
| | acetonitrile | | | 3.407 | 0.203 | 2.870 | 0.141 |
| p-AMP (P_CS ) | gas phase | 2.617 | 0.060 | 4.223 | 0.077 | 3.495 | 0.075 |
| | cyclohexane | | | 4.097 | 0.116 | | |
| | chloroform | | | 4.067 | 0.118 | 3.277 | 0.074 |
| | dichlormethane | | | 4.067 | 0.116 | | |
| | acetonitrile | | | 4.079 | 0.111 | 3.273 | 0.071 |
| Pyridine (Par_C1) | gas phase | 3.700[a] | 0.052 | 4.651 | 0.077 | 4.175 | 0.054 |
| | cyclohexane | | | 4.519 | 0.104 | | |
| | chloroform | | | 4.479 | 0.106 | 4.036 | 0.067 |
| | dichlormethane | | | 4.474 | 0.106 | | |
| | acetonitrile | | | 4.480 | 0.103 | 4.039 | 0.066 |

[a] Second transition

**Table 4** CIS(PCM)/aug-cc-pVDZ calculated values of transferred charges (|e|) from respective donor to TCNE, dipole moments (Debye) of the complexes both in the ground and first excited states

| Donor molecule (complex structure) | Solvent | $\Delta q_{GS}$ [\|e\|] | $\mu_{GS}$ [D] | $\Delta q_{ES}$ [\|e\|] | $\mu_{ES}$ [D] |
|---|---|---|---|---|---|
| Aniline (AN2) | gas phase | 0.120 | 1.90 | 0.838 | 10.67 |
| o-AMP (M1) | gas phase | 0.161 | 1.95 | 0.914 | 10.91 |
| | cyclohexane | 0.170 | 2.14 | 0.976 | 12.34 |
| | chloroform | 0.175 | 2.32 | 1.034 | 13.68 |
| | dichloromethane | 0.176 | 2.47 | 1.061 | 14.31 |
| | acetonitrile | 0.177 | 2.53 | 1.086 | 14.93 |
| m-AMP (T1 ) | gas phase | 0.180 | 3.49 | 0.930 | 11.90 |
| p-AMP (P1) | gas phase | 0.139 | 3.87 | 0.968 | 13.52 |
| pyridine (Par_C1) | gas phase | 0.121 | 2.64 | 0.956 | 12.68 |
| | cyclohexane | 0.126 | 2.91 | 0.986 | 13.83 |
| | chloroform | 0.128 | 3.15 | 0.992 | 14.62 |
| | dichloromethane | 0.129 | 3.27 | 1.021 | 15.24 |
| | acetonitrile | 0.130 | 3.40 | 1.031 | 15.68 |

explained within PCM model: with increase of solvent polarity there is increase of amount of transferred charge. The same is true for both ground state and equilibrated CT excited state. Even explanation of the fact that the ratio of the slopes of these two linear dependences is not equal to the ratio of the transferred charges in these states (i.e., 0.85/0.15=~6 for charges in gas phase) is straightforward. According to PCM model based, which is based on solution of Poisson equation for solute in dielectric, due to interaction between induced charges on surface of the cavity and the charges in the solute. Higher polarity of the solvent increases values of induced charges which, in their turn, increase polarization of the solute. This fact causes in CT complexes increased amount of electron transfer from donor to acceptor.
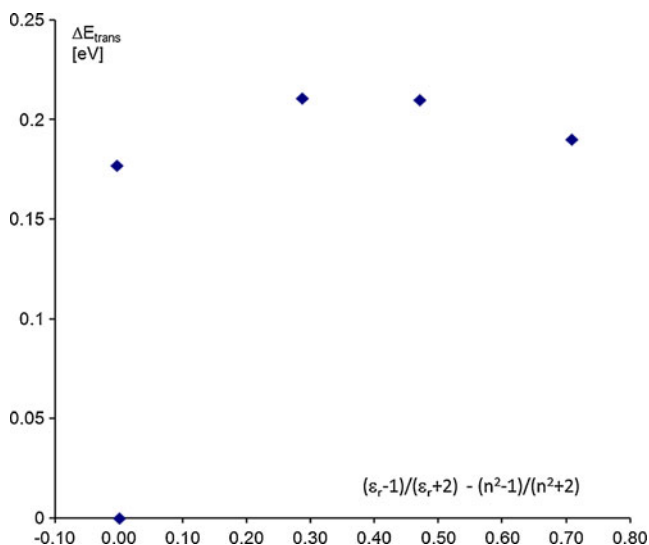
## Conclusions

The results on calculations of electronic absorption transitions of representative series of TCNE complexes of aminopyridines (aniline, o-, m-, p- aminopyridines and pyridine itself) are accomplished by a non-empirical CC2 as well as both CIS and LC-corrected TD-DFT (LC-BLYP) methods. From calculated values one can conclude that CC2 non-empirical method including solvent shift corrections made by PCM (CIS) is very suitable to adequate description of absorption bands positions and their intensity in these chemically rather unstable complexes. Also stability or more precisely, the intermolecular interaction energy between particular donor and TCNE acceptor is fairly described by both CC2 (MP2) and DFT-D approaches. Both intermolecular interaction
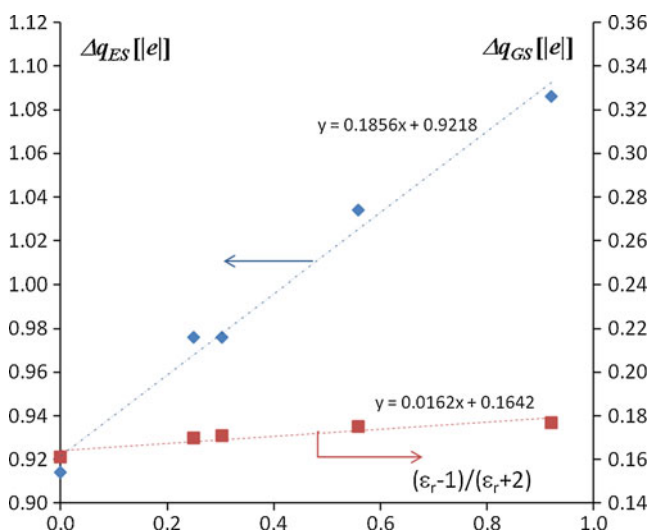


**Fig. 3** Dependence of red solvent shifts for Aniline – TCNE complex (An_Cs minimum) on solvent polarity, CIS(PCM) calculations in non-equilibrium model



**Fig. 4** Transferred charge (|e|) in the ground (right axis) and excited (left axis) states as a function of solvent polarity for M1 minimum of o-AMP – TCNE complex

energy and the energy of the first and second π-π* CT transitions is governed by the value of the first IP in the respective donor. Thus, both the above quantity as well as the first ionization potential are results of π- electron donor amino group and electron acceptor aza- group in particular donor. Aza- substitution enhances IP of o-, m-, and especially p- aminopyridines (in the above ordering) compared to aminobenzene (aniline) while it also enhances IP of pyridine relatively to benzene itself. Quite interesting is the different complex formation in pyridine – TCNE system where both π and perpendicular σ(n) complexes are formed with almost the same intermolecular interaction energy. More than that, in the case of σ(n)- complex the energy of n-π* transition (3.67 eV) is lower than that of π−π* transition (3.70 eV) though energy of n-orbital is under energy of two π- (HOMO, HOMO-1) orbitals in pyridine.

The present particular study we regard as an introduction to application of quite precise quantum chemical methods to the broad field of biologically interesting and very active compounds such as substituted aminopyridines. We feel that to achieve calculated accuracy better than ± (0.1-0.2) eV at prediction of electronic transition energies in CT complexes the inclusion of solvent effect is needed at least at the CIS (PCM) level. As to basic, i.e., gas phase calculations of transition energies still more rigorous approaches as CC2 are needed.

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