
Theoretical Analysis of the Electronic Ground and Excited Franck–Condon State of 2-Alkylamino-(3, 5, or 6)-Methyl-4-Nitropyridine N-oxides

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*Remembering Jurek Prochorow
and many years of common work*

We theoretically characterised properties of the electronic ground and excited Franck–Condon state of 2-alkylamino-(3, 5, or 6)-methyl-4-nitropyridine N-oxides. The obtained results of time-dependent density functional theory calculations are consistent with the experimental absorption spectra. The nature of the lowest excited states of the considered N-oxides molecules is discussed. Two excited singlet states (in the midst of four lowest states) have the charge-transfer character. These states have different charge-transfer contribution of the two electron donor groups to the same electron acceptor. In consequence, different conditions for the promotion of intramolecular proton transfer in excited state are created in each case.

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1. Introduction

The N-oxides investigated in this work, namely: 2-alkylamino-(3, 5, or 6)-methyl-4-nitropyridine N-oxides (see Fig. 1 for the structure and abbreviations for particular molecules) belong to the class of intramolecular electron–donor–acceptor (EDA) systems with electron donor and electron acceptor groups being connected through the π -electron aromatic system.

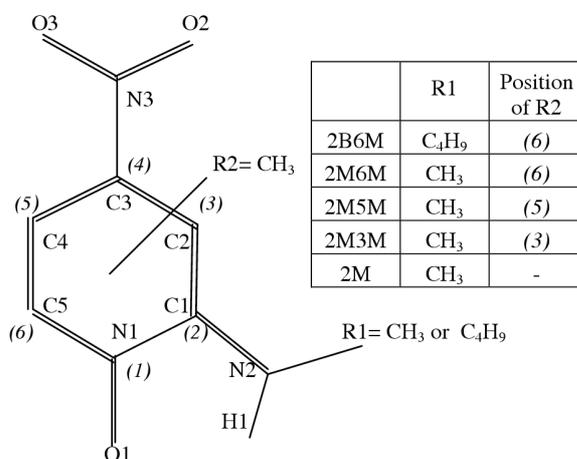


Fig. 1. The structure and abbreviations for molecules considered in this work. In parenthesis and in italic — denotations of the positions of atoms in aromatic ring are shown.

The characteristic features of all the EDA systems are the low-lying charge-transfer (CT) states related to the transfer of electronic charge from the donor to the acceptor. The concept of CT states and transitions was introduced and advanced by Mulliken in his theory of intermolecular complexes [1]. Verification of this theory on the base of both, theoretical and experimental, researches of many molecular systems was continued through the second half of the last century. These researches were conducted in many scientific centers [2–5], among others by the Prochorow group [6–9]. Various molecular complexes in different experimental conditions were investigated in order to elucidate intermolecular interactions leading to the charge transfer between electron donor and electron acceptor moieties. Another aim was to establish the medium impact (viscosity, polarity, rigidity, etc.) on this kind of processes. An interest with molecules, in which donor and acceptor are linked through a single bond or through a bridge of a conjugated double bond, or by the π -electron aromatic system, has also appeared [10–17]. This has given a start to the question on the nature of interactions in intramolecular EDA systems.

Recognition of photophysics of the CT reactions is an important step in understanding the excitation energy dissipation pathways in molecular systems and has become a predominating one with the passage of time. New concepts appeared, as for example, the exciplex formation [2, 18] or excited state proton transfer reactions driven by the charge-transfer process [19, 20]. Solving the photophysics of intramolecular EDA systems led to the opening of a large discussion and different models on structure relaxation connected with the intramolecular charge-transfer (ICT) process have been proposed: twisted intramolecular charge transfer (TICT) or planar, wagged, and rehybridized ICT (i.e. PICT, WICT, and RICT) [10, 12–17].

In recent decade a great deal of attention was devoted to electro-optical properties of intramolecular EDA systems which are directly connected to their charge-transfer nature [21–24]. Among different molecules, derivatives of 4-nitropyridine N-oxide fall into this group [22]. Some of EDA systems showing the dual fluorescence can be used in the fabrication of molecular switches [21]. The N-oxides molecules, under considerations, show the dual fluorescence, too [20, 25, 26].

The photophysics of the investigated by us N-oxides seems to be very complicated, in correspondence to their structure. The titled N-oxides have two donor groups, $>NO$ and the $-NHC_nH_{2n+1}$, combined with one acceptor group $-NO_2$ and simultaneous intramolecular hydrogen bond $N2-H1 \dots O1$ between the atoms of both donor groups (see Fig. 1). The fluorescence spectra are composed of normal and anomalous (with large Stokes shift) bands [20, 25, 26]. Both, absorption and fluorescence, spectra are strongly solvent dependent [20, 25, and 27]. The non-negligible differences between the absorption and fluorescence excitation spectra and the quantum yield value that is the excitation wavelength dependent were detected in nonpolar and aprotic solvents [26].

Appearance of the anomalous fluorescence band was interpreted in terms of excited state intramolecular proton transfer (ESIPT) between the amino NHR_1 and the NO group [20]. This process was estimated as a very fast one in polar solvents and described as being triggered by creation of the excited intramolecular CT state. From the other hand, in nonpolar medium such process was shown to be much slower [25, 26]. An interesting conclusion was drawn out, namely, it was suggested that the observed excitation wavelength dependence of the quantum yield is due to existence of the two different intramolecular proton transfer processes [26].

The crystal structure of considered N-oxides was described only for 2B6M [25] and for 2-ethylamino-4-nitropyridine N-oxide (2E) molecules [28]. In both cases the crystal packing takes place with participation of intermolecular hydrogen bonds but in the case of 2B6M, the molecule crystallises in the especially beautiful form of a double hydrogen-bonded dimer, which consists of two internally hydrogen-bonded monomers [21].

Results of theoretical calculations concerned with different properties of amino-substituted 4-nitropyridine N-oxides were presented occasionally and chaotically. Namely, electronic spectra of 2M3M and 2M5M were calculated by intermediate neglect of differential overlap (INDO) method [27] whereas dipole moments of the same molecules were calculated by means of vectorial summation of the group moments and by *ab initio* Hartree-Fock (HF) 3-21G method [29]. The density functional theory (DFT) B3LYP/6-31G(d,p) method was used for calculation of IR spectrum of 2-ethylamino-4-nitropyridine N-oxide [28] and electronic spectrum of 2B6M [20, 25]. The RHF/6-311G++(d,p) method was used in the studies on acid-base interactions for 2M6M [30]. The single data on the vertical transitions between the ground state (S_0) and the first

excited singlet state (S_1) obtained by CIS/6-311G(d,p) and time-dependent (TD) DFT/def-TZVP methods were also showed [20].

Here we report the results of more systematic calculations, concerning the structure and electronic absorption spectra for some N-oxides, differentiating by the position and lengths of the two alkyl substitutes (compare Fig. 1). Calculations were performed at the TD DFT B3LYP/6-31G(d,p) level. We discuss the character of transitions to the lowest electronic excited states and the conditions for the ES IPT reaction in their internal hydrogen bond of the N–H...O type (see Fig. 1).

2. Calculations

Ground-state geometry optimisation of all investigated molecules was performed at the DFT B3LYP/6-31G(d,p) level employing the Gaussian 98 program package [31]. Geometry optimisation was followed by calculations of the vibrational frequencies in order to verify whether the obtained stationary points are true minima or not. Energies of electronic transitions and corresponding oscillator strengths (for the structure optimised in the ground state) were calculated by TD DFT B3LYP/6-31G(d,p) method. Due, only to the ground state optimization, the interpretation of the excited state properties is limited to the non-equilibrated Franck–Condon excited states. Nevertheless, these states are very important as the primary states from which the molecule may further evolve to equilibrated excited states.

3. Results

3.1. Ground state optimised geometry

The ground state geometry optimisation was performed for all five investigated molecules. Possibilities of verification of the calculated geometrical structures by the corresponding experimental data are limited, however it was shown previously [21] that the DFT B3LYP/6-31G(d,p) optimisation correctly reproduces the experimental structure of 2B6M molecule. The same conclusion concerns to the results obtained for 2E molecule [28].

In the light of these findings we can believe that geometries of other presented here molecules are also correct. Comparison of the results obtained for the five investigated N-oxides permits to conclude that with the exception of 2M3M molecule the structure of other N-oxides can be described as planar. In the case of 2M3M, displacement of the nitro group from the best plane is found to be 19° . This result can be compared to previously investigated structure of 2-nitramino-3-methyl pyridine N-oxide where this angle is even larger, 70.80° [32]. Displacement of the nitro group is probably connected with steric hindrance of this group with the methyl group in position (3) (see Fig. 1). However, such effect was not found for 2M5M molecule with the methyl group that is also located in the *ortho* position with respect to the nitro group. This discrepancy can be understood in terms of stronger steric effects of the methyl group in the case of 2M3M since in

this molecule the methyl group is placed between the NO_2 and the NHCH_3 group. It must be added, however, that the displacement of the nitro group was found for 2M5M within the framework of semiempirical calculations [27] and by means of *ab initio* calculations on RHF/6-31G(d,p) level [33]. Hence, experimental results are required for definitive verification of such discordant theoretical results.

Steric effect of the CH_3 group in 2M3M is also demonstrated by differences in the calculated geometry of the intramolecular hydrogen bonding. The results of calculations indicate that $\text{N2-H1}\dots\text{O1}$ hydrogen bond is coplanar with the aromatic ring in all the molecules with exception of 2M3M. In the case of 2M3M molecule, the N2-H1 bond composes the angle 5° with the ring plane. Moreover, the $\text{N2-H1}\dots\text{O1}$ angle in this molecule is 116° in comparison to 110° for the rest of molecules. Differences are concerned also with the $\text{H1}\dots\text{O1}$ bond length. It is the shortest in 2M3M (1.95 \AA) as compared with that in other molecules (2.03 \AA).

3.2. Electronic spectra

The results of calculations of electronic transitions for all investigated N-oxides together with some available experimental data (all these results are obtained from the measurements in solutions) are collected in Table I. A nice agreement between the calculated and experimental findings is observed although the bands determined experimentally have a relatively large width (compare absorption spectrum of 2B6M shown in Fig. 2). This, in turn, makes a precise determination of transition energies to be impossible. From these reasons an alternative procedure [35] for comparison of calculated results (represented by simulated spectrum) with experimental data is applied.

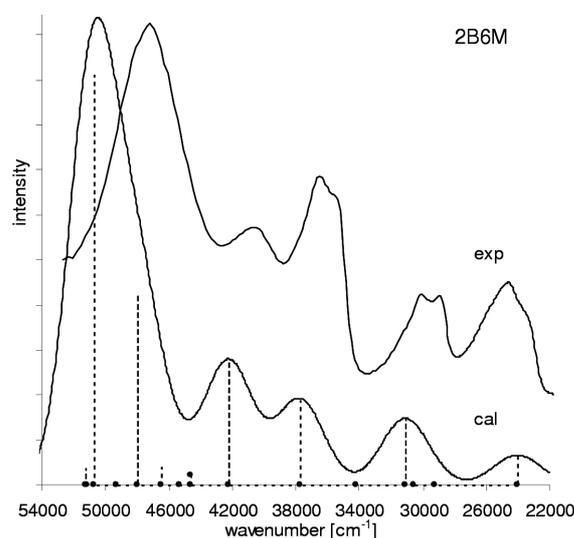


Fig. 2. Simulated (cal) and experimental (exp) absorption spectra of 2B6M molecule. Dots represent calculated energies of the electronic $S_0 \rightarrow S_i$ transitions while the vertical lines — their oscillator strengths (see the text for further details).

TABLE IA

Transition energies ΔE (in cm^{-1}) of the electronic $S_0 \rightarrow S_i$ transitions and their oscillator strengths (f) calculated with TD DFT B3LYP/6-31G(d,p) method.

2B6M				2M6M				2M5M-	
cal		exp	cal		exp	cal		exp	
ΔE	f	ΔE [20,25]	ΔE	f	ΔE [34]	ΔE	f	ΔE [27]	
24022	0.066	23696	24184	0.069	23786	24013	0.069	24510	
29287	0.000		29323	0.000		29213	0.000		
30605	0.000		30646	0.000		30018	0.000		
31099	0.148	28985	31155	0.144	28968	31788	0.153	30488	
		30120			30102				
34196	0.000		34177	0.000		34200	0.000		
37741	0.190	35460	37844	0.175	35612	37396	0.198	34843	
		36496			36683			35971	
42206	0.271	40650	42391	0.223	40584	41724	0.263	39841	
44609	0.023		45122	0.006		44548	0.070		
45304	0.000		45388	0.000		45397	0.000		
46505	0.039		46504	0.035		46195	0.039		
48032	0.420		48237	0.450		47617	0.196		
49291	0.000		49357	0.000	47169	49089	0.000		
50754	0.913		50924	0.829		49629	0.000	47619	
51144	0.000		51094	0.000		50606	0.952		
51249	0.036		53164	0.020		52567	0.089		

The simulated absorption spectrum is constructed replacing the calculated vertical lines, representing the oscillator strength of the particular $S_0 \rightarrow S_i$ transitions, with the Gaussian contours with the 1000 cm^{-1} width. Hence, such spectrum can be used for comparison with broad and diffused experimental spectra. The result is presented in Fig. 2. It is seen that the both spectra are similar despite that reproduction of the intensity distribution is not an excellent one.

Simulated spectra of all the investigated N-oxides are displayed in Fig. 3. It is seen that in general the spectra of the whole group of molecules have a similar character and it is possible to say that essentially the spectrum of 2-alkylamino-4-nitropyridine N-oxide is composed of the five bands. In the case of 2M3M however, the band at about 40000 cm^{-1} is weakly visible. On the basis of the results shown in Fig. 3 one can conclude as follows:

— in practice, the lengths of the R_2 substituent in the $-NHR_2$ group do not have any influence on the electronic spectra of the molecules under consideration,

TABLE IB

2M3M			2M	
cal		exp	cal	
ΔE	f	ΔE [27]	ΔE	f
25302	0.067	25907	24300	0.072
29332	0.029		29139	0.000
30193	0.009		30544	0.000
32164	0.095	30030	31838	0.130
34181	0		34124	0.000
36809	0.244	36232	37512	0.260
40498	0.107		42272	0.206
43121	0.019		44550	0.000
43870	0.003		45643	0.006
46064	0.054		46214	0.053
46645	0.195		48994	0.260
47075	0.066	46512	49300	0.000
48100	0.521		50152	0.000
49531	0.054		51656	0.832
51054	0.009		53363	0.000

— substitution of the R_1 in different positions of the aromatic ring leads to a slightly changed absorption spectrum; the energy order of the first band within the considered group is as follows: $E(2M5M) < E(2M6M) < E(2M3M)$.

These conclusions are in line with the experimental data [22, 27] including the “lack” of band at about 40000 cm^{-1} for 2M3M molecule (compare Table I). Our calculations indicate that this ”lack” is formal and results from the overlap of the neighboring contours corresponding to different electronic transitions.

It is worthwhile to note that such facts confirm validity of theoretical approach undertaken in this case and deepen the analysis of spectral nature of particular excited state of the series under consideration. In Fig. 4, the diagrams of the energy levels of 2M and the two “parent” molecules, namely 4-nitropyridine N-oxide (A) and 2-N-methylaniline-4-nitropyridine (B) are presented. The shapes of particular molecular orbitals involved in transitions to the lowest excited electronic states together with electronic configurations that contribute to the particular transitions are also demonstrated. It is obvious that a good correspondence exists between the shapes of lowest unoccupied molecular orbitals (LUMO) of all molecules (i.e. $L(2M) \sim L(A) \sim L(B)$) and likewise between the low lying highest

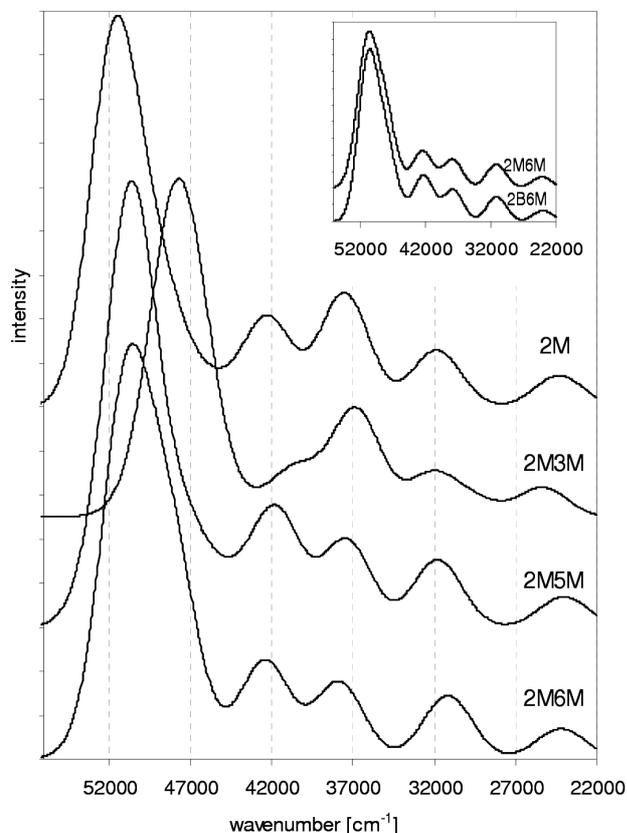


Fig. 3. Absorption spectra calculated for 2M6M, 2M5M, 2M3M, and 2M molecules. Inset: absorption spectra calculated for 2M6M and 2B6M molecules.

occupied molecular orbitals (HOMO) (i.e. $H-2(2M) \sim H-1(A) \sim H-1(B)$ and $H-3(2M) \sim H-1(A) \sim H-1(B)$). Generally, the two highest HOMO orbitals of 2M (H and $H-1$) are the combinations of the highest orbitals of A and B. Hence, in the first approximation, from the energetic point of view, the following relations can be proposed: $H(2M) \sim H(B)$ and $H-1(2M) \sim H(A)$.

In Table II, characteristics of the lowest energy electronic transitions are demonstrated. It is evident that two transitions in 2M molecule with the non-zero oscillator strengths, namely: $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_4$ can be correlated with excitations $H \rightarrow L$ in B (2-N-methylaniline-4-nitropyridine) and A (4-nitropyridine N-oxide) molecules, respectively. Both these transitions can be characterised as intramolecular CT transitions. This is shown in Fig. 5 where the changes of charge on the particular groups of molecules on electronic excitations to the S_1 , S_2 , S_3 , and S_4 states are displayed. One may notice that the $S_0 \rightarrow S_1$ transition in 2M can be essentially described as the transition that takes place from the methylamino ($-NHCH_3$) group to the nitro ($-NO_2$) group while the $S_0 \rightarrow S_4$ is the transition

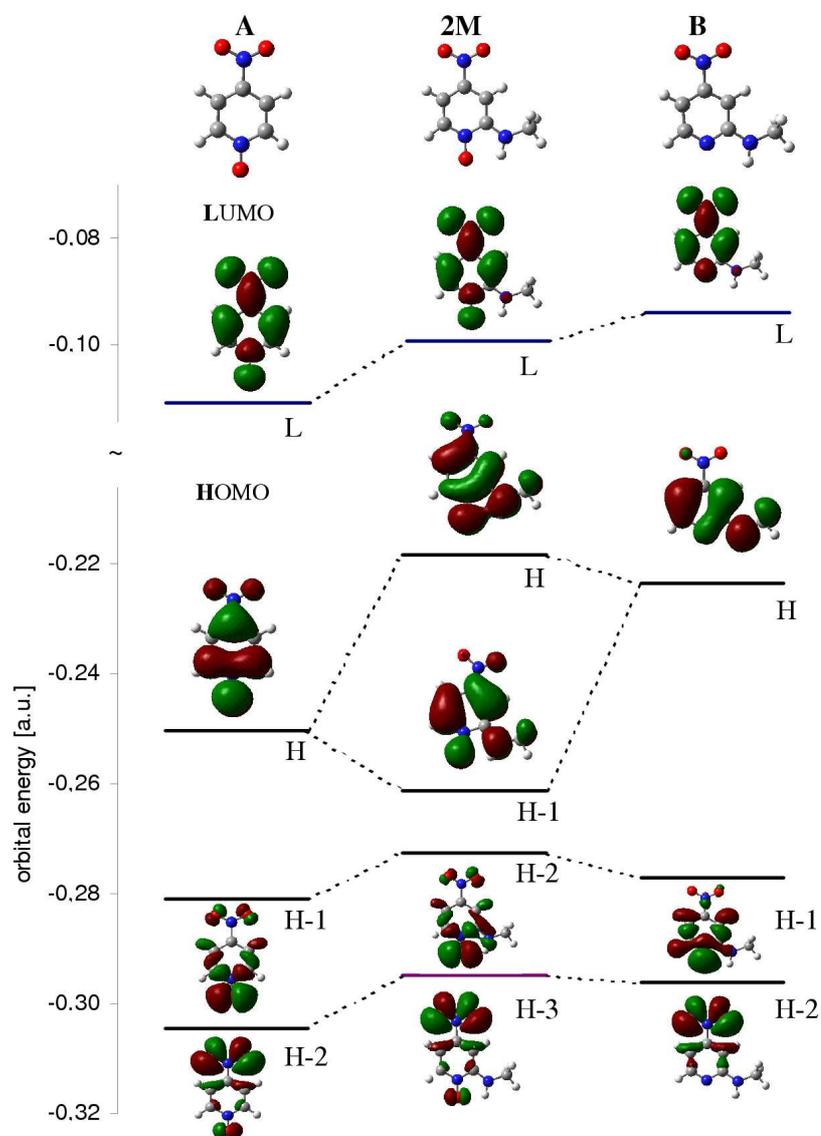


Fig. 4. Diagram of the energy levels and shape of corresponding molecular orbitals for 2M and 4-nitropyridine N-oxide (A) and 2-N-methylaniline-4-nitropyridine (B).

that occurs from the NO group to the $-\text{NO}_2$ group. Two other transitions in 2M, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$, that are dark in 2M5M and 2M6M but of a low intensity in 2M3M (where the NO_2 group is not coplanar with the ring) are described in terms of a double combination of the same two electronic configurations (see Fig. 4). The contribution of the $-\text{NHCH}_3$ group to these transitions in practice is rather negligible (see Fig. 5).

TABLE II

Characteristics of the electronic transitions of the lowest energy for 2M, A, and B molecules (compare Fig. 4) (ΔE — transition energy in cm^{-1} , f — oscillator strengths, and CI — the most important electronic configuration contributing to the given transition).

A			2M			B		
ΔE	f	CI	ΔE	f	CI	ΔE	f	CI
27569	0.000	H-1 \rightarrow L	24301	0.007	H \rightarrow L	23720	0.002	H \rightarrow L
			29139	0.000	H-2 \rightarrow L -H-3 \rightarrow L			30201
30085	0.000	H-2 \rightarrow L	30545	0.000	H-3 \rightarrow L H-2 \rightarrow L	32557	0.000	H-1 \rightarrow L
31851	0.034	H \rightarrow L	31839	0.013	H-1 \rightarrow L			

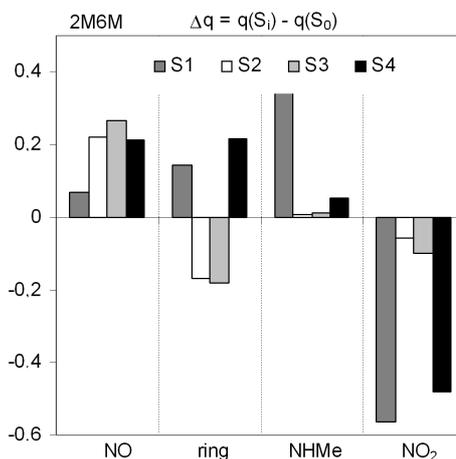


Fig. 5. Changes of the charge distribution on particular groups of 2M6M molecule: NO, ring, NHCH₃, and NO₂ at electronic excitations from S_0 to the S_1 , S_2 , S_3 , and S_4 states. It is seen that the NO₂ group plays role of an acceptor in the transitions to S_1 and to S_4 states. The donor groups in the transition to the S_1 are NHCH₃ and in the less degree the aromatic ring. In the case of the transition to the S_4 state the charge displacement takes place from both, the NO group and aromatic ring, to the NO₂ group.

The CT character of the $S_0 \rightarrow S_1$ transitions in 2M is not surprising in view of similarity of this transition to the $S_0 \rightarrow S_1$ transition in B molecule and simultaneously to the well known CT character of nitroanilines, confirmed in the literature both by experiment and theory [21–23, 36]. The same note concerns to the $S_0 \rightarrow S_4$ transition in 2M molecule, which can be compared to the CT state of 4-nitropyridine N-oxide molecule [22, 37].

TABLE III

Dipole moments (in D) in the ground S_0 and excited S_i states of 2M calculated without and with the relaxed terms (for the details see text). Calculations method — TDDFT/6-31G(d,p).

S_0	3.29	
	unrelaxed	relaxed
S_1	13.36	9.24
S_2	8.18	2.32
S_3	6.90	5.78
S_4	11.97	6.54

The CT character of the $S_0 \rightarrow S_i$ and $S_0 \rightarrow S_4$ transitions should be reflected by the corresponding increase in the dipole moment in S_i and S_4 states in comparison to the ground (S_0) state. This is shown in the first column of Table III for 2M molecule. Important growth of the dipole moment in both, S_1 and S_4 , states is obvious; however, the received values of dipole moments remain the problem for further explanation. It is known that the estimation of dipole moments in electronic excited states, especially within the DFT, still rests the calculation problem [38]. Generally, terms representing the orbital relaxation should be included. As yet, this is unattainable for DFT method within the Gaussian package. Hence, we have checked the effects of these terms using the Turbomole package [39] including the appropriate procedure. The corresponding results are given in second column of Table III. It is seen that dipole moments calculated with relaxation terms (relaxed) are of smaller values than dipole moments obtained without them (unrelaxed). However, though these differences, the conclusion about the CT character of the S_1 and S_4 states of 2M remains unchanged, i.e. a large dipole moment of the S_1 state and somewhat smaller one of the S_4 state but both of them are larger in comparison to those in the ground state. Finally, it can be added that the experimentally observed solvent shift of the first absorption band ($S_0 \rightarrow S_1$ excitation) of 2B6M is larger than the shift of the second band ($S_0 \rightarrow S_4$) [25] which confirms the calculated relation between dipole moments in both, S_1 and S_4 , excited states.

The results, shown in Fig. 5, allow us to draw an additional important conclusion. The changes of charge distribution on excitation to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_4$ states are not equivalent for interactions in the intermolecular hydrogen bonding N2–H1...O1. The displacement of charge taking place in the $S_0 \rightarrow S_1$ transition acts in direction of reinforcement of the hydrogen bond in excited state while an opposite effect may be expected in the case of $S_0 \rightarrow S_4$ transition. This fact together with the close neighbourhood of two dark states (S_2 and S_3) near the S_1 and S_4 states indicates that modeling of excitation decay pathways and

a full explanation of violation of the Kasha–Vavilov rule observed [26] for the investigated N-oxides is a serious task. Presently, we continue work on this issue by studying the excited states potential energy surfaces of the considered N-oxides.

4. Summary

The results showed in this work clearly indicate the intramolecular CT nature of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_4$ transitions in 2-alkylamino-(3, 5, or 6)-methyl-4-nitropyridine N-oxides. In each of them the transfer of charge occurs practically from only one donor group to the same acceptor, the nitro group. This fact is important from the point of view of the ESIPT process taking place between the two donor groups. The changes of electronic distribution on the molecule in the case of $S_0 \rightarrow S_1$ transition reinforce the excited state intramolecular hydrogen bonding while in the case of $S_0 \rightarrow S_4$ transition it is reverse. The situation is further complicated by the presence of two dark states (S_2 and S_3) as adjacent to the radiative states S_1 and S_4 . It is expected that a complicated image of photophysics of 2-alkylamino-(3, 5, or 6)-methyl-4-nitropyridine N-oxides that results from the experiment [20, 25, 26] might be possible to be explained only when all the above factors will be taken into consideration.

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