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Computational Spectroscopy of a Bichromophoric Molecule, 2-Methyl-1,2,3,4-tetrahydroisoquinoline, in Solutions[1]

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An ab initio calculation of the title molecule was performed to interpret previously observed electronic spectra of the title system. Since the computation concerns the isolated molecule, possible effects of solvent molecules had to be taken into account, especially for such as Rydberg states. The $S_3 \leftarrow S_0$, $S_2 \leftarrow S_0$, and $S_1{}^n \leftarrow S_0$ absorption bands are (re)assigned to the excited states of the L_b, L_a/CT, and $n_N\sigma^*$ (3s) states, respectively. The minor $S_1{}^a \leftarrow S_0$ absorption observed at the red area of the $S_1{}^n \leftarrow S_0$ band in acetonitrile is reinterpreted as being a $n_N\pi^*$ (CT) state. Correspondingly, the π, nN, and aN fluorescence spectra are (re)ascribed to the excited states of the L_b, $n_N\sigma^*$, and $n_N\pi^*$ states, respectively. The $n_N\sigma^*$ and $n_N\pi^*$ states are found to be restricted to the equatorial and axial conformers, respectively. The exceptionally long progression of the π fluorescence in hexane is interpreted as being due to the closeness of the L_a and L_b states.

As reviewed by us[2–5] (especially in Ref. 5), the several aromatic amines in polar solvents, such as acetonitrile, had been shown to be ionized monophotonically forming geminate ion pairs with solvent molecules through fluorescent states. To interpret this fact, the so-called charge-transfer-to-solvent (CTTS) state (the terminology originally defined as a Rydberg state in the solution) was postulated as an intermediate state. However, the geminate ion pair, itself, could also be regarded as a sort of the CTTS state, i.e. an excited state belonging to a cluster composed of a solute molecule and solvent molecules. This is one of the reasons why we started an investigation of the title molecule, 2-methyl-1,2,3,4-tetrahydroisoquinoline (NMTHIQ), i.e. a peculiar aliphatic amine. The relationship with a twisted intramolecular charge-transfer (TICT) state, as observed in systems such as (dimethylamino)benzonitrile (DMABN) in polar solvents, was also noted.

Though various observations had been reported in our previous papers,[4–6] this paper/computation aims to interpret four kinds of absorption bands and three kinds of fluorescence spectra, as described in the abstract. Among 20 possible combinations of four possible conformers (as described with four combinations consisting of the two kinds of conformations, i.e. half-chair & half-boat conformations of the aliphatic side and the two orientations, i.e. equatorial & axial orientations of the CH_3 group relative to the aliphatic ring) and five possible electronic states (S_0, $3s \leftarrow n_N$, CT, L_b, and L_a states), 8 combinations were confirmed to exist (by CIS, for the isolated molecule). The conformer in the ground state was mostly half-chair equatorial (eq), with a minor contribution of half-chair axial (ax) in acetonitrile. Thus, all three absorption bands are ascribed to the eq conformer, with a minor contribution of the ax conformer for the red-edge band in acetonitrile only. With the possibility of an interconversion between the eq and ax conformers in the excited states, as was actually discerned by time-resolved spectroscopy,[5,6] the fluorescence spectra may have contributions from both conformers. However, the nN and aN fluorescence spectra were found to be exclusively attributed to the eq and ax conformers, respectively.

1. Experimental Facts to Be Interpreted

In the above abstract and introduction, the description of the major conclusion to be derived in the text is already made. In this section, however, a further explanation of the experimental data is made in order to clarify the subsequent discussion, as extracted from those in previous papers.[4–6]

1.1 Absorption and Fluorescence (Excitation) Spectra in Hexane. As shown in Fig. 1 (the same as Fig. 1a of Ref. 4) as the Curve 1, three lower bands are evident in the absorption spectrum of hexane (n-H): (1) A band at 240–280 nm is typical of the L_b band (its 0, 0 band being located at 36450 cm^{-1}); (2) Its shoulder at 270–310 nm (with the 0, 0 at 33300 cm^{-1}) was "tentatively" assigned to the CT band due to its significant solvent effect on the intensity distribution; (3) A weak band at 300–350 nm (29500 cm^{-1}) was assigned to the $3s \leftarrow n_N$ band by extrapolation of those in various kinds of aliphatic amines. Figure 2a (taken from Ref. 4) represents fluorescence (excitation) spectra in n-H. The dual π and nN fluorescence is evident as bands at 270–410 and 340–460 nm, respectively. With approximate mirror-image relationships, these are assigned to the same excited states as those of bands 1 and 3 in the absorption spectrum, i.e. the L_b and 3s states, respectively. It was noted that the progression of the π fluorescence in n-H is longer than those in any other media, including methanol (MeOH) and acetonitrile (AN).[5] No such long progression was observed for the parent molecule, 1,2,3,4-tetrahydroisoquinoline (THIQ), in any media.[4,5]

1.2 Absorption and Fluorescence (Excitation) Spectra in Acetonitrile. Curve 3 in Fig. 1 represents the absorption spectrum in AN. Except for the second band of the shoulder area (and the red-tail of the first band not being evident in the figure), the shape of the spectrum is apparently the same as that in n-H. Therefore, the assignments were the same as those in n-H. Figure 2c represents the fluorescence (excitation) spectra in AN. In this case, the π fluorescence is almost missing. Instead of this,

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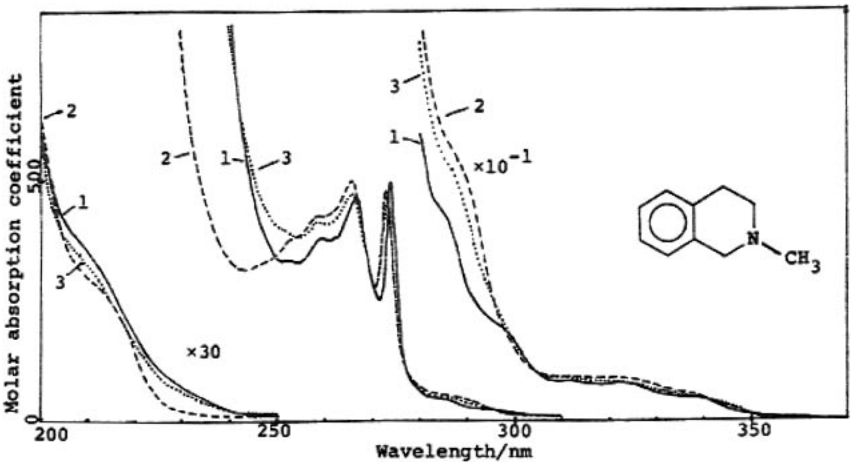

Fig. 1. Absorption spectra of NMTHIQ in *n*-H (1), MeOH (2), and AN (3).

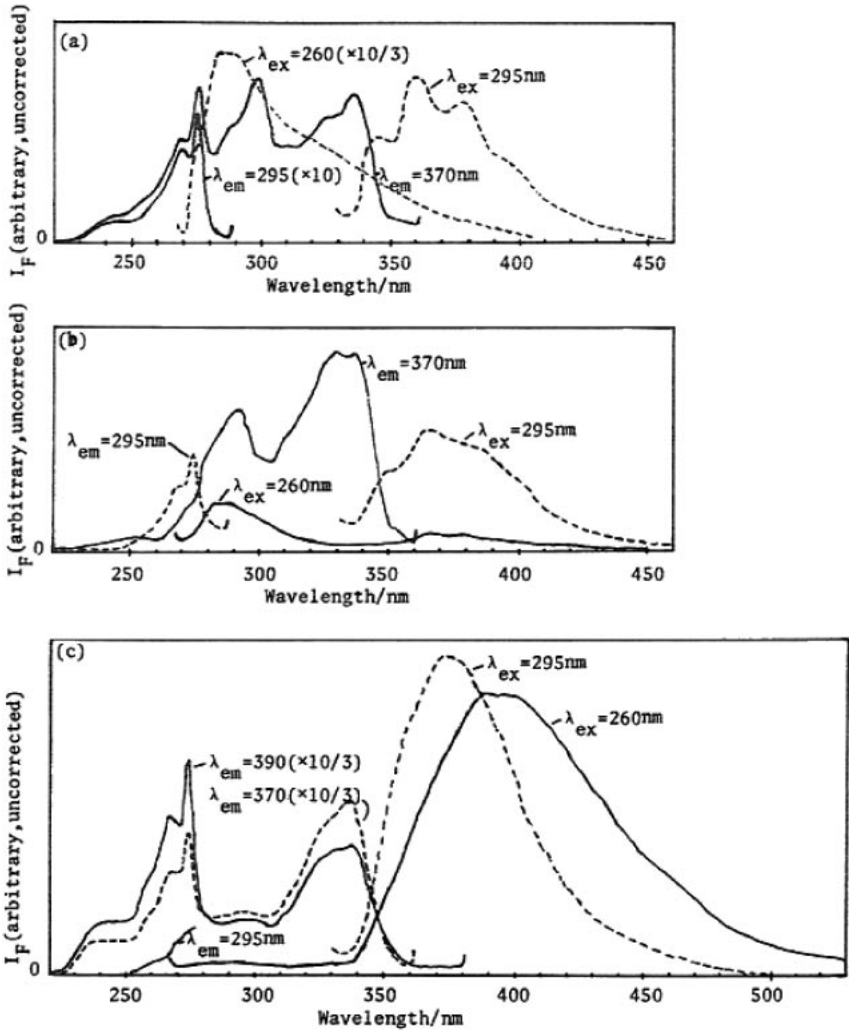

Fig. 2. Fluorescence (excitation) spectra of a 6.7×10^{-4} M solution of NMTHIQ measured after N_2 gas bubbling in *n*-H (a), MeOH (b), and AN (c).

the dual *n*N and *a*N fluorescence spectra are noticeable as overlapped bands at 340–460 and 370–530 nm, respectively. An examination of the excitation spectra for both emissions reveals that a much weaker red-tail portion of the $S_1 \leftarrow S_0$ band (the 0, 0 at 27000 cm^{-1}) can be ascribed to the minor (anomalous; to be distinguished from normal) component of the ax conformer being existent even in the ground state of NMTHIQ in AN.

2. Computation

A computation was performed with Gaussian 98 suites of programs.[7] Firstly, a search for stationary points (potential minima) was made by optimization (Opt) with CIS/RHF along with an option of Gen, i.e. using combined basis sets of 6-31G(d, p) (for C and H) and 6-311G(d, p) (for N). This particular combination of CIS/Gen appears to be the best for the initial search with our facility. As described in introduction, eight kinds of potential minima were found: S_0(eq), S_0(ax), S_1(L_b, eq), S_1(L_b, ax), S_1(L_a, eq), S_1(L_a, ax), S_1(3s, eq), and S_3(“CT”, ax). The symbol 3s (as already introduced in abstract) is an abbreviation of the $n_N\sigma^*$ (3s $\leftarrow n_N$) state; “CT” indicates that it is not a pure intramolecular CT state of a $n_N\pi^*$ type, but rather its admixture with others, such as $n_N\sigma^*$ (not restricted to the 3s) and $\pi\pi^*$ types.

For the ground state, two conformers (eq & ax) are noted. As for the excited states, the most noteworthy is the coexistence of five potential minima in the lowest excited state, separated from each other in the adiabatic multi-dimensional potential surface of S_1. (It has to be noted that the symbol S_n ($n = 1$–3) in this section is not always consistent with those in abstract, introduction, and the preceding section, which have been used for conventional routine work of the spectral assignment. Furthermore, these double notations are used throughout this paper, depending on the occasion.) This finding would indicate congestion of the lower excited states with a complex structure of potential surfaces that consist of avoided crossing, seams, and funnels. To clarify this situation, transient states (TSs) were sought with the option of such as QST2. Two, six, and one TS were found for the S_0, S_1, and S_3 states, respectively. Besides these, vertical (de)excitation (VE/VD) energies from the potential minima were calculated to “predict” the locations of the Franck-Condon (FC) maxima in the electronic spectra, i.e. to reproduce the observed Stokes shift between the absorption and fluorescence spectra corresponding to the geometrical change upon (de)excitation. (From this information for VE, being shown in Chart 1 with the left-super-

	axial			equatorial	flat (C_s)
	^{vi}3s’s(ax) ~78700			^{vi}3s’s(eq) ~77400	
	^{vi}3s(ax) 78400			^{vi}CT’s(eq) ~74200	^{v5}3s(A') 75100
	^{vi}CT’s(ax) ~68400			$^{v4}B_a$(eq) 66800	
	S_3(‘CT’,ax) 61310			$^{v3}B_b$(eq) 66400	
					$S_2(L_x,A')$ 54980
					$S_1(L_b,A')$ 53890
$S_1(TS^{\mathbf{a}}_b$,ax) 52410		$S_1(TS^{\mathbf{a}}_e,L_a)$ 52760			$S_1(3s,A'')$ 53420
	$^{v2}L_a$(ax) 51390			S_1(3s,eq) 51730	
	$S_1(L_a$,ax) 50160	$S_1(TS^{\mathbf{a}}_e,L_b)$ 51770	$S_1(TS^{\mathbf{a}}_b$,eq) 51380	$^{v2}L_a$(eq) 51400	
	$^{v1}L_b$(ax) 50080			$^{v1}L_b$(eq) 50100	
	$S_1(L_b$,ax) 49740			$S_1(L_a$,eq) 49990	
				$S_1(L_b$,eq) 49050	
				^{v0}3s(eq) 37530	
	^{v0}’CT’(ax) 9900				
	$^{v0}L_a$(ax) 9010			$^{v0}L_a$(eq) 6430	$S_0(A')$ 4880
	$^{v0}L_b$(ax) 1870	$S_0(TS^{\mathbf{a}}_e)$ 2750		$^{v0}L_b$(eq) 1100	
	S_0(ax) 740			S_0(eq) ≡ 0	

Chart 1.

script vi ($i > 0$), to be described below, the starting point for Opt of the excited state could be selected.) Also to be mentioned is the fact that the difference of the (VE/VD) energy from that of the corresponding minimum is a measure of the geometry change upon (de)excitation. (For example, the broadness of the 3s and "CT" band with relatively large Stokes shifts can be interpreted with this, as described below.) Though the computed values (with CIS/Gen) are not precise enough (compared to those with CAS/6-311G(d, p) and others), most of the (acquired and important) energy values (/cm^{-1}) for these levels are listed below (Chart 1; as a set of simplified versions of potential curves to mimic true multi-dimensional potential surfaces of this system): The first thing be noticed concerning the above "Chart" is its horizontal "axis", which may be regarded as the simplest possible route of a geometrical change extracted from the complex multi-dimensional potential surface. Emphases were made for the 8 minima, as already described. The pair of symbols, (a, b) and (a, e), as superscripts/subscripts for the TS of interconversion indicate (L_a, L_b) and (ax, eq), respectively. The symbols v0 and vi (i representing S_i), as the left superscripts attached to the labels of excited states, correspond to the FC maxima for VD and VE involving the indicated excited states, respectively. As indicated by the bold superscript at the right, the geometry/wavefunction of the TS is mostly closer to that of the "reactant" than to that of the "product". The TS at the flat geometry belonging to the point group C_s was easily attained just by the simple Opt (due to its small degree of freedom), and worked as a starting point to reach at the potential minimum with the corresponding eq geometry. Though the CIS method does not fully take the effect of electronic correlation (ECr) into account, several important conclusions can be drawn from this list (Chart 1):

(1) In the ground state, the population of the ax conformer is predicted to be small (as confirmed with MP2 and CAS, vide infra), unless the effect of (the polar) solvent is taken into account.

(2) As already mentioned, congestion of the lower excited states is evident with the L_b, L_a, 3s (and CT) states. (Therefore, a CASSCF calculation is also performed, as described below.)

(3) As can be seen with a remarkably high location of ^{v0}3s(eq), the geometry of the 3s state is quite different from those of all other 7 states, as identified above (vide infra).

Related to the last observation, the pair of frequencies of the vibrational modes around the NCH_3 group (calculated with Freq) are given in Table 1 along with the N–C(H_3) bond length ($R_{N\text{–}Me}$, with Opt), for the 8 kinds of minima. A more detailed description will be made later concerning this observation. Apart from some systematic variations (most of which are not discussed in this paper), a significant elongation of $R_{N\text{–}Me}$ in the 3s state is noteworthy, while reducing the frequencies of the N–CH_3 out-of-plane (o-o-p) bending and the CH_3 torsional modes and allowing for them to be treated as large-amplitude modes, as indicated in the Table. (These may ultimately be described as an N-inversion and internal-rotation, respectively, corresponding to the G_6 molecular symmetry group (MSG) beyond the C_s(M) MSG.[8]) These facts clearly correspond to the characteristic of its σ^* orbital, as described later with a Figure.

At this stage, it has to be noted that the computation of the electronic states of some benzene analogs, like *N*-methylpyrrole (NMP) with such as CIS/6-31(1)G(d, p), tends to favor the L_b state over the Rydberg state, which is not absolutely consistent with that by such as CAS/6-311G(d, p).[8,9] Two reasons may be found for this:

Table 1. Structural Information (Bond Length and Frequencies of Lower Modes) of NMTHIQ at Various Potential Minima Obtained with the CIS = (Root = 1 or 3) (or RHF)/Gen (See Text for the Detail of Gen.) and CAS(10, 8, NRoot = 1 or 2)/6-311G(d, p) (in the Parentheses)

State	$R_{N\text{–}Me}$/pm	N–CH_3 o-o-p/cm^{-1}	CH_3 torsion/cm^{-1}
S_0(eq)	144.4 (144.5)	91 (85$^{a)}$)	257 (251$^{a)}$)
S_0(ax)	144.9 (144.9)	85 (80$^{a)}$)	214 (215$^{a)}$)
S_1(L_b, eq)	144.4 (144.5)	84 (76)	254 (254)
S_1(L_a, eq)	144.6 (144.5)	73 (74)	255 (250)
S_1(L_a, ax)	144.9 (144.9)	83 (85)	207 (218)
S_1(L_b, ax)	144.9 (144.9)	83 (80)	252 (257)
S_1(3s, eq)	235.3 (—)	23 (—)	17 (—)
S_3("CT", ax)	143.9 (—)	93 (—)	137 (—)

a) The values with MP2/6-311G(d, p) are exposed, those with CAS(10, 8, NRoot = 1)/6-311G(d, p) not being available for these. (See text for the detail.)

(1) Many Rydberg orbitals are available nearby the HOMO in both NMTHIQ and NMP, especially with 6-311G(d, p), to allow for perturbations of such as ECr.

(2) The splitting of the L_a and L_b states is already attained by the CIS in both molecules, just like in benzene.

To endorse the above conclusions (by CIS) and to see which kinds of (excited) states are mainly lowered by such as an ECr effect, i.e. (1) by expanding the basis set for MO and (2) by taking account of the higher order CI's, CASSCF calculations were carried out, with a partial success. A stepwise procedure was taken for the CAS, while expanding the functional space, i.e. through such as CAS(8, 7, NRoot = 2)/6-311G(d, p). Table 2 is a list of optimized energies/minima acquired with an option of CAS(10, 8, NRoot = 2 or 1)/6-311G(d, p). Corresponding experimental data are also attached.

Firstly, as evident in this Table 1, optimization of 3s and "CT" states was not successful, at least with this option. Also, other trials, such as by further expansion of the functional space, e.g. with CAS(12, 9, NRoot = 2)/6-311G(d, p), turned out to be too slow to accomplish the job, by means of the facilities accessible to the author. This observation itself may be taken as evidence of the fact that the error in the calculation with CIS/Gen due to such an ECr effect is larger for these states than the other states, as given in the Table, in spite of the likely belief that the promotion of one of the localized pair of electrons in the n_N orbital to the diffuse orbital reduces the ECr energy. This appears to be strongly associated with another observation that the upper orbitals (HOMOs: highest occupied molecular orbitals in the excited states) in these states have significant contributions from the diffuse components of the basis set. This was confirmed by an examination of the output, as may be discerned in the figures of HOMOs to be shown later.

Secondly, the primary geometry of the S_1(L_a, ax) state optimized with the above option as the last step of the automatic stepwise procedure happened to be a mere TS with an imagi-

Table 2. Energy Terms as Optimized with CAS(10, 8, NRoot = 2 or 1)/6-311G(d, p)

Electronic State	E/hartree	ΔE/cm^{-1} (calcd)	ΔE/cm^{-1} (obsd)
$S_1(L_b, ax)$	−440.687697	38980	—
$S_1(L_a, ax)$	−440.687872	38940	33500?
$S_1(L_b, eq)$	−440.691451	38150	36450
$S_1(L_a, eq)$	−440.691519	38140	33300
$S_0(ax)$	−440.858591	1470	—
$S_0(eq)$	−440.865294	≡ 0	≡ 0

nary frequency, as was confirmed by Freq. Therefore, a manual trial-and-error operation was required to find out the potential minimum, as given in the Table, where a slight inversion between the L_a and L_b levels is evident through the change from CIS to CAS. In this respect, it should also be noted that the other $S_1(L_a, eq)$ state, among $6 - 1 = 5$ states, is more stabilized with CAS (relative to that of CIS, while consuming more machine time) than the other 4 states, indicating more stabilization corresponding to the greater contribution of the diffuse orbitals. Actually, an examination of the wavefunctions elucidated that the peculiar $S_1(L_a, ax)$ state partially shares common electronic configurations (ECfs, with the CT character) with the S_3("CT", ax) state (vide infra).

Another (minor) observation is a prediction of a slight abundance of the ax conformer (especially in the vapor phase). It should be noted that, for the Opt of the ground state, the following route was most economical: RHF/Gen → RHF/6-311G(d, p) → MP2/6-311G(d, p) → CAS(10, 8, NRoot = 1)/6-311G(d, p). Furthermore, our facility suffered from a "malloc" error for the Freq after the final Opt in the route. Therefore, the values for the ground state in the Tables (computed with CAS) are based on the assumption that these geometries represent potential minima. Accordingly, the values of the frequencies for the ground state (with [a)]) given in the Table 1 are taken from those computed with MP2/6-311G(d, p).

Finally, the polarized continuum model (PCM) calculation[7,10] (as requested by one of the referees) was performed (at the optimized geometry of the free NMTHIQ) with an additional Keyword, such as SCRF = (CPCM, Solvent = 17 or 19) (for hexane or acetonitrile, respectively), whose results predicted no solvent effect, even with Opt for the peculiar case of the $S_1(L_a, ax)$ state. This is not an unexpected result, but is rather in conformity with the experimental observation of a small solvent effect on the adiabatic transition energies, the absolute value of the difference being below 100 cm^{-1} regardless of the sign. Therefore, a PCM calculation was also performed for the lowest FC states, approximately identified with the $^{v1}L_a$(eq) and $^{v1}L_a$(ax) states (Table 3, different from the case of CIS calculation as shown in the Chart 1) to which the observed red shift of ~300 cm^{-1} (while changing the solvent from hexane to acetonitrile; Fig. 1) might correspond. It could also be interpreted, however, as being due to an overlapped contribution from both conformers in the case of the acetonitrile solution, the splitting of the 0, 0 bands being assumed to be ~200 cm^{-1}. As is evident in Table 3, little stabilization was observed for the both of the FC states with Solvent = 17 (approximately representing hexane). In contrast, stabilization as much as 400 and 450 cm^{-1} was observed with Solvent = 19 for the $^{v1}L_a$(eq) and $^{v1}L_a$(ax) states, respectively. This is what can be interpreted as being a manifestation of the usual solvent effect (with no need to appeal to the overlapping) to which the PCM method is applicable. However, the most significant fact is that the PCM model did not work for lowering the location of the L_a state more than that of the L_b state, i.e. for interpreting the observed spectra as a whole, including its media effect. This is one of the facts to be discussed in the next section.

Table 3. VE Energies (/Hartree) Corresponding to the Potential Minima, S_0(eq) and S_0(ax) in the Three Kinds of Circumstances by CAS(10, 8, NRoot = 2)/6-311G(d, p) with or without SCRF = (CPCM, Solvent = 17/19)

	$^{v1}L_a$(eq)	$^{v1}L_a$(ax)
in vapor	−440.677362	−440.677099
Solvent = 17	−440.677362	−440.677099
Solvent = 19	−440.679257	−440.679146

As described in section **1** of Experimental Facts, the assignments were made with three kinds of excited states (L_b, CT, and 3s) all of them with both eq and ax conformations. However, in this computation, we acquired 6 kinds of minima that are not always coincident with the above. The most noteworthy is concerned with a pair of S_1(3s, eq) and S_3("CT", ax) states. Apparently, they refuse coexistence with each other (at the same geometry). This is incompatible with the above assignments of two conformers (eq and ax) for every kind of state. To obtain some idea on this subject, Figures 3 and 4 are presented to show the MOs involved in the excitations in these states for the optimized geometries. The LVMO (for the lowest vacant molecular orbital and not to be confused with either HOMO or LUMO) represents the MO where one electron was removed, while HOMO indicates the MO into which the electron is promoted.

In the case of the 3s state, the n_N orbital of LVMO in Fig. 3 is a 2p-type orbital located mainly on the N atom with some distribution over the adjacent carbon atoms. A slight extension to the π orbital of the benzene ring is also noted. On the other hand, the shape of the 3s orbital is quite different from what may be imaged based on its name. Namely, to call it as a σ^* orbital (or N–CH_3 anti-bonding orbital) would be more adequate.

As to Fig. 4 of the "CT" state, the situation is more complicated. The n_N orbital is again a $2p_N$-type orbital oriented approximately in parallel with the molecular plane, but mixed up with the ring π orbital with a ratio of ~1:1, and with a minor distribution over the adjacent carbon atoms. While the π^* orbital is mostly distributed over the benzene ring, it has to be noted, however, that the contribution of this ECf upon the total

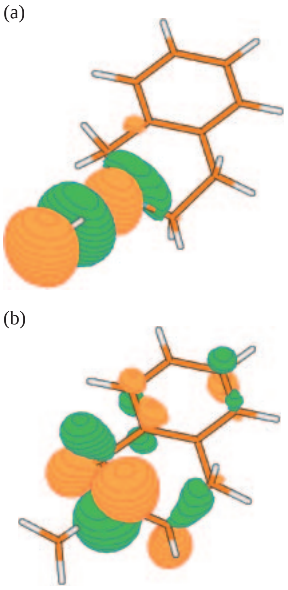

Fig. 3. The (a) HOMO (3s, 41) and (b) LVMO (n_N, 40) of the $n_N\sigma^*$ (3s) state at the geometry optimized as a S_1 state.

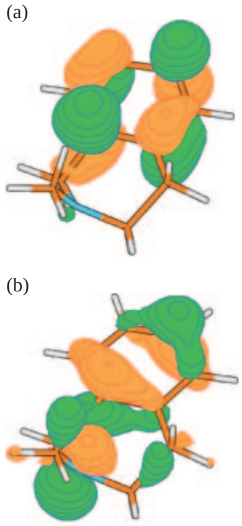

Fig. 4. The (a) HOMO (π^*, 41) and (b) LVMO (n_N, 39) of the $n_N\pi^*$ (CT) state at the geometry optimized as a S_3 state.

wavefunction of the present S_3 state is 32%, accompanied by contributions from many other ECfs (including those for higher Rydberg states), as already mentioned. Among the other ECfs, the largest contribution of 8% was from that representing the L_a-type S_1 state with the common HOMO of Fig. 4(a), for this geometry. This would indicate a considerable ECr energy in these states, especially in the "CT" state, which should not be the S_3 state any longer. However, lowering of this state by CAS would not be big enough to reach the real S_1 for the assignment of the absorption band (the 0, 0 band at 29500 cm^{-1}). Therefore, the solvent effect must be taken into account for a quantitative interpretation of both bands and others in a form to take over the PCM model, as will be done in the next section.

3. Interpretation of the Experimental Data

In a previous series of papers,[4–6] the assignments of electronic spectra were made by means of the spectroscopy in both frequency[4] and time[5,6] domains, while taking account of the possible media effects, i.e. dependencies on nonpolar, polar, protic, and acidic media. Thus, speculation was required for the final decision. This time, a new kind of information is available with the ab initio calculation, namely the information of available excited states of NMTHIQ in the isolated condition. However, as described in the preceding section, this information does not exactly predict the spectra, even for the molecule in nonpolar solvent, *n*-H. This is particularly applied to those involving excited states with a significant contribution from the diffuse orbital, as mentioned above. Actually, it must be related to the existence of the conduction band in the liquid (located below the vacuum level), regardless of its properties, such as polarity. For example, the ionization potentials of most molecules in media are known to be lower than those in a vapor by as much as 1 eV. Correspondingly, the energy levels of the Rydberg states (in aliphatic amines) are lowered as brought in media. This fact must be taken into account for assigning the spectra.

Firstly, we recall the number of excited states of NMTHIQ required for the assignments. Namely, to interpret the four absorption bands of the $S_3 \leftarrow S_0$, $S_2 \leftarrow S_0$, ${S_1}^n \leftarrow S_0$, and ${S_1}^a \leftarrow S_0$ transitions and three fluorescence bands of the π, *n*N, and *a*N types, at least four kinds of states have/had to be assumed, counting conformers, while the normal and anomalous components were solely ascribed to eq and ax, respectively. On the other hand, the theoretically available excited states were counted to be six, distinguishing conformers.

Now, the announced "assignments" were made stepwise, from the easier towards the more difficult/speculative ones: With similarities of the spectral shapes to such as toluene,

(1) there is no doubt concerning the assignment of the L_b state to both $S_3 \leftarrow S_0$ and π.[4] With no other candidate and by extrapolation of the spectral data of aliphatic amines,

(2) the assignment of the 3s ($n_N\sigma^*$) state to both ${S_1}^n \leftarrow S_0$ and *n*N is also maintained.[4]

The large Stokes shift between them can easily be interpreted by the difference of the geometries between 3s and S_0.

The $S_2 \leftarrow S_0$ absorption band, whose spectral shape is sensitive to the media, had been ascribed to the CT state.[4] However, the present calculation (by CIS) obtained only one sort of the CT state, i.e. the highly located S_3("CT", ax) state, as restricted to the conformation ax. Though the energy of this state could be lowered by the solvent effect, as described below, it can hardly interpret the full observation, as was described above, and deserved a further discussion. Thus,

(3) the L_a state is left as a candidate for the assignment of the $S_2 \leftarrow S_0$ band. Why is the location of the L_a state lower than that of the L_b state (as much as 3000 cm^{-1}, much larger than what was estimated by the present CAS calculation; Table 2)? As mentioned in the preceding section, this can be interpreted as being due to the predominant interaction among the benzene part, the aliphatic amine part, and solvent molecules in their L_a state over that in their L_b state, due to such

as larger ECr energy. (The failure of the PCM method does support the involvement of the LUMO in the solvent molecule.) Thus, a more suitable definition of this state can be made as the L_a/CT state, CT indicating both of the $n_N\pi^*$ and CTTS states. This interpretation reminds us of other systems, such as aminonaphthalenes and indole derivatives in polar media.[1–3,6] Also, in polar media, the ax conformer of NMTHIQ might have some contribution to the observed $S_2 \leftarrow S_0$ absorption band area while borrowing the intensity from such as the B_a band, as guessed by an examination of the output with CAS (though not predicted by the PCM calculation, vide supra). This assignment is also given in Table 2 with a ? mark. Thence,

(4) the S_3("CT", ax) state remains as the only candidate for the pair of $S_1{}^a \leftarrow S_0$ and *a*N. Their broad band structure can easily be interpreted by taking account of the vibration modes of solvent molecules. Though the energy level of the former is located very high by CIS, its significant stabilization by the polar solvent molecules has to be recognized, as the only one choice being left for the interpretation, while suggesting a contribution of such as the ECf of the CTTS state to this state. This fact is reminiscent of the TICT state, as encountered in such as the acetonitrile solution of DMABN. Namely, though not well recognized in the literature so far,[4–6] the TICT state may also be contributed from the CTTS state, like in the case of the L_a/CT state just mentioned above. Related to the above set of assignments,

(5) a reply to the possible question has to be made: Why does violation of Kasha's rule occur with the two kinds of fluorescence regardless of the conformers?

An answer can be given easily by pointing out the multi-dimensional potential surface of the S_1 state with 5 (or 6; in the polar media such as acetonitrile, AN) potential minima (Chart 1). Namely, in the present system, the "internal conversion" between the lower (fluorescent) excited states (in view of the conventional spectroscopy) is nothing but the interconversion through/over the potential barrier within the S_1 state, with little room for the nonadiabaticity operator to be invoked. Another problem to be solved is

(6) the long progression of the π fluorescence, as observed only in hexane. This can be interpreted either (i) as overlapped emissions from both the L_a and L_b states communicating with each other or (ii) as a vibronic coupling between the L_b and L_a states nearby $S_1(TS^a{}_b$, eq). In conformity to the experimental observation, both effects are lessened in polar media due to a significant change of the structure in the L_a state (towards the L_a/CT state), causing its geometrical departure from the L_b state.[5] All of the required "assignments" for the excited state were made as above. However, one more point has to be made concerning the ground state:

(7) Why is ax abundant in polar media particularly in acetonitrile ($<10\%^5$)? This is against the prediction for an isolated molecule as well as that by the PCM method, as described above. However, this can be interpreted as being due to the contribution of the ECf of the CTTS state into the S_0(ax) state, i.e. a mixing of the 3s-type ECf, whose HOMO is distributed over the solvent molecules, ANs (another interpretation of the "contact" CT interaction between the solute and solvent molecules).[1,5,6]

4. Concluding Remarks

Before concluding, a remark is made concerning the experimental data on THIQ[4,11] (as requested by one of the reviewers). In the final section of Ref. 4, we made the following statement: Similar solvent effects are found in bichromophoric molecules, THIQ, *N*-methyl-4-phenyl-1,2,3,6-tetrahydopyridine (MPTP), *N*-methyl-4-phenylpiperidine (NM4PP), and 4PP with decreasing significance in descending order. The reasons for the extremely brief description of THIQ are:

(1) We could not completely remove the impurity, isoquinoline (IQ) in THIQ.[4]

(2) The ax conformer is abundant even in the nonpolar solvent, hexane. This is consistent with the present ab initio calculation, as also applied to THIQ. Therefore,

(3) no quantitative discussion could be made like what was done for the case of NMTHIQ. Judging from our experience, as described above, we can make our own assessments concerning the experimental data in Ref. 11:

(1) They did overlook the $S_1{}^{nN} \leftarrow S_0$, $S_1{}^{aN} \leftarrow S_0$ absorption bands as well as the $S_1{}^{nN} \rightarrow S_0$ fluorescence band, which apparently exist in their own spectral data. It seems that they were disturbed by the impurity, IQ.

(2) Since the excitation spectrum of the anomalous *a*N fluorescence has the component ascribable to the $S_1{}^{aN} \leftarrow S_0$ absorption, their assignment of this emission to the TICT state is misleading.

In the above section, the assignments of the electronic spectra were successfully made. However, it was based on specific assumptions concerning the solvent effect, as was speculated in the previous sections. Therefore, more experimental and theoretical studies are required.

The most desired experiment may be time-resolved spectroscopy at the time scale of ps. For example, we may extract the π fluorescence of the L_a type that might be hidden in the total π fluorescence, as is ascribed solely to the L_b state in this paper. (The previous trial to observe the "CT" fluorescence was a failure by conventional spectroscopy.[4]) This scheme was actually implied in the preceding section as being one of the possibilities for interpreting the long progression of the π fluorescence in the *n*-H solution.

As for a theoretical study, the first thing to do would be to perform a theoretical calculation of the isolated NMTHIQ with a better facility (such as a supercomputer) so that the difficulties encountered in the present study could be partially removed, so as to acquire better solutions for the isolated molecules, including those of the $n_N\sigma^*$ and $n_N\pi^*$ states. However, the most desired study is presumed to be an ab initio calculation of the electronic states of a cluster that consists of one NMTHIQ molecule and tens of solvent molecules, with a supercomputer, though any other model-calculations (such as by regarding the media as the continua which receives the (excess) electron. However, to correct/lower the location of the CTTS state with the factor $\varepsilon/\varepsilon_0$ is apparently an over-estimation, ε and ε_0 being dielectric constants of the media and vacuum, respectively, for it has to be regarded more like the $n_N\sigma^*$ state.) may also be made, depending on the available resources. Actually, this kind of approach has been made for an aqueous solution of iodide ion.[12]

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