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Proton transfer reaction in 2-hydroxy-3-formyl benzoic acid at room temperature and 77 K and some study on AM1 potential surfaces

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Abstract

Proton transfer processes in 2-hydroxy-3-formyl benzoic acid (2HFBA) have been studied by means of absorption and emission spectroscopy in some non-polar and weakly polar solvents at room temperature and 77 K in relation to 4-hydroxy-3-formyl benzoic acid (4HFBA). The excited state intramolecular proton transfer (ESIPT) is evidenced by a large Stokes shifted emission (10,500 cm^{-1}) due to the formation of enol tautomer of 2HFBA in non-polar solvents. In 1,4-dioxane and tetrahydrofuran, 2HFBA forms hydrogen bonded complex while both tautomer and hydrogen bonded complex have been detected in benzene. Unlike 4HFBA, 2HFBA forms hydrogen bonded complex in presence of a base, like triethyl amine in non-polar solvents due to the rupture of intramolecular bond. Moreover, 2HFBA shows phosphorescence even in absence of base on lowering the temperature to 77 K. The energetics of the ground and excited state proton transfer in 2HFBA have been studied at the AM1 level of approximation. The ground singlet is predicted to have a large activation barrier on the proton transfer path while the barrier height is much lower on the corresponding excited singlet surface.

Keywords: Proton transfer; Hydrogen bonding; Semi-empirical calculations; Potential energy surface

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1. Introduction

In our earlier work, we have studied the ground and excited state proton transfer processes of 4-methyl-2,6-diformyl phenol (MFOH), 3-methyl-6-hydroxy-m-pthalic acid (HmPA) and 4-hydroxy-3-formyl benzoic acid (4HFBA) [1–4]. It has been established that in non-polar solvents, the most stable species in the ground state is the normal primary closed form and that in the excited state is the tautomeric form. It has also been suggested that in molecules where both inter- and intramolecular proton transfer (PT) occur together, it can represent an important non-radiative channel either to products or to the ground state. The rate could be high enough to make the PT competitive with inter system crossing and lead to photochemical products. The non-polar environment offers an excellent opportunity for investigating the proton transfer reaction of the unsolvated molecules. Due to the absence of solvent perturbation, PT is rapid in non-polar solvents [5,6]. The proton transfer of aromatic molecules which are intramolecularly hydrogen bonded in the ground state, undergo marked changes depending upon the kind of substituents present on the aromatic ring and carbonyl group [7–10]. In our earlier work on proton transfer reaction we observed significant changes in spectroscopic properties of such compounds depending upon the nature of the substituents [2,3,11–14]. In the case of MFOH, intermolecular hydrogen bonded complex or open conformer was formed from the enol tautomer in the excited state due to the rupture of the intramolecular bond on the addition of TEA [1]. However, in the case of 4HFBA, the tautomer band remained almost unaffected by the added TEA [4].

The significant observation about the changes in the luminescence property, at 77 K and the mechanism of such changes seems to merit further investigation. Nagaoka et al. [15,16] suggested that benzaldehyde type of molecules without intramolecular bond, i.e. the open conformer is likely to be produced after irradiation and on lowering the temperature

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to 77 K. It was suggested that phosphorescence occured from the open conformer and due to the rotation of the formyl group. In non-polar solvents, we have detected phosphorescence in the case of MFOH, but we were unable to detect phosphorescence in the case of 4-methyl-2,6-diacetyl phenol (MAOH) in pure non-polar solvent at 77 K. However, phosphorescence appeared in the case of MAOH in presence of a base. This shows that pure non-polar solvent cannot rupture the intramolecular hydrogen bond in the case of MAOH. The rotation of the formyl group is necessary for the occurance of phosphorescence. At 77 K, 4HFBA exhibited phosphorescence in pure dioxane, but in 3-methyl pentane and *n*-hexane, phosphorescence occurred only in the presence of a base [4].

For further information, we have synthesized 2HFBA in the Department of Inorganic Chemistry of this institute. In this present work, we have reported the results of room temperature as well as low temperature spectroscopic properties of 2HFBA in some non-polar and electron donor solvents along with some theoretical results.

The recent literature is replete with studies devoted to the analysis of excited state proton transfer (ESPT) in organic compounds both from theoretical and experimental points of view [17–19]. Although ab initio calculations involving extended basis sets with extensive configuration interaction (CI) have been successful in predicting the energetics, structures, and reactivities of organic molecules in the ground and excited state, semi-empirical molecular orbital methods, such as MNDO and AM1 also provide good estimation of geometries of such molecules and insight relating to reaction paths of chemical changes that they undergo [20].

It was shown earlier that intramolecular hydrogen bond length data determined from AM1 calculations were fairly close to the X-ray crystallographic results [5]. The AM1 calculations have been known to describe the energetics and topographics of hydrogen bonded systems fairly accurately [21]. In our earlier work [5], we have reported a theoretical investigation on the proton transfer reaction of 4-methyl-2,6-diformyl phenol (MFOH) in a semi-empirical framework. We have determined the molecular structures of MFOH in the ground (S_0) and excited (S_1) electronic states using the AM1 method of approximation. In this paper, we have determined the molecular structures of 2HFBA in the ground (S_0) and excited (S_1) electronic states at the AM1 level of approximation. The kinetics and energetics of proton transfer in both the states have been determined at the AM1 level. The calculations ultimately lead us to the construction of potential energy surfaces on which the proton transfer is supposed to take place.

2. Experimental

MFOH, 4HFBA and 2HFBA were prepared in the Inorganic Chemistry Department of this institute in a similar way to that reported earlier [12,13]. The compounds were recrystallized from methanol and dried before use. The solvents, namely cyclohexane, *n*-hexane, *n*-heptane, benzene, 1,4-dioxane and tetrahydrofuran (THF) were of spectroscopic grade and were all dried and distilled before use. Analytical grade triethyl amine (TEA) was used as a strong base. All the solvents were checked for purity by steady state fluorescence measurements.

Absorption, emission and excitation spectra were recorded on a Shimadzu UV-2401 PC UV–vis recording spectrophotometer and Perkin-Elmer MPF 44B spectrophotometer, respectively. The low temperature emission spectra were recorded on a HITACHI spectrophotometer model F4500. The concentration of 2HFBA was maintained at $\sim 2–4 \times 10^{-5}$ mol dm^{-3}. All other experimental details are same as reported earlier [1]. The energetics of the ground and excited state proton transfer in 2HFBA have been investigated at the AM1 level of approximation as carried out by the MOPAC package, version 6.0 for Windows.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of 2HFBA exhibit a single band at 330 nm in all the non-polar and weakly polar solvents like *n*-heptane, cyclohexane, *n*-hexane, benzene, 1,4-dioxane and tetrahydrofuran (THF). On the addition of a strong base like triethyl amine (TEA), the 330 nm band shifts to 338 nm with an increase in intensity of the band (Fig. 1). The 330 and 338 nm bands can safely be assigned to the primary normal closed form, N (N1, N2) and hydrogen bonded complex, HC (HC1, HC2) of 2HFBA, respectively as shown in Fig. 2 and as reported earlier in the case of MFOH and 4HFBA [1–4]. The intermolecular hydrogen bonded complex is formed due to the interaction of 2HFBA and TEA. It is worth mentioning here that in the case of MFOH, the absorption spectra remain unaffected by the added base in the solvents used here [1]. Similar observations have been made in the case of 4HFBA also [4].

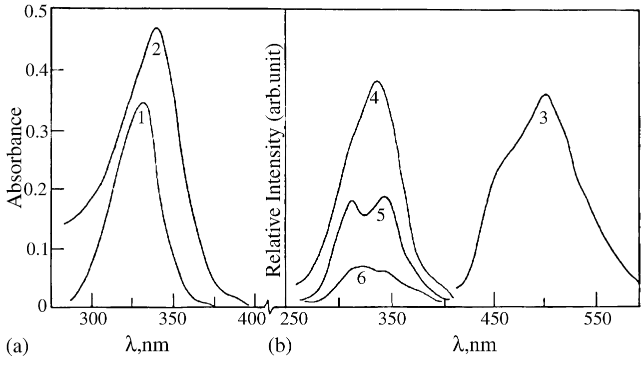


Fig. 1. Absorption (a: 1,2), emission (b: 3) and excitation (4–6) spectra of 2HFBA. a: 1 (dioxane), 2 (dioxane+TEA); b: 3 (benzene); 4 (dioxane+TEA), 5 (dioxane), 6 (cyclohexane). $\lambda_{mon} = 440$ nm (4,5) and 505 nm (6). $\lambda_{exc} = 330$ nm (3).

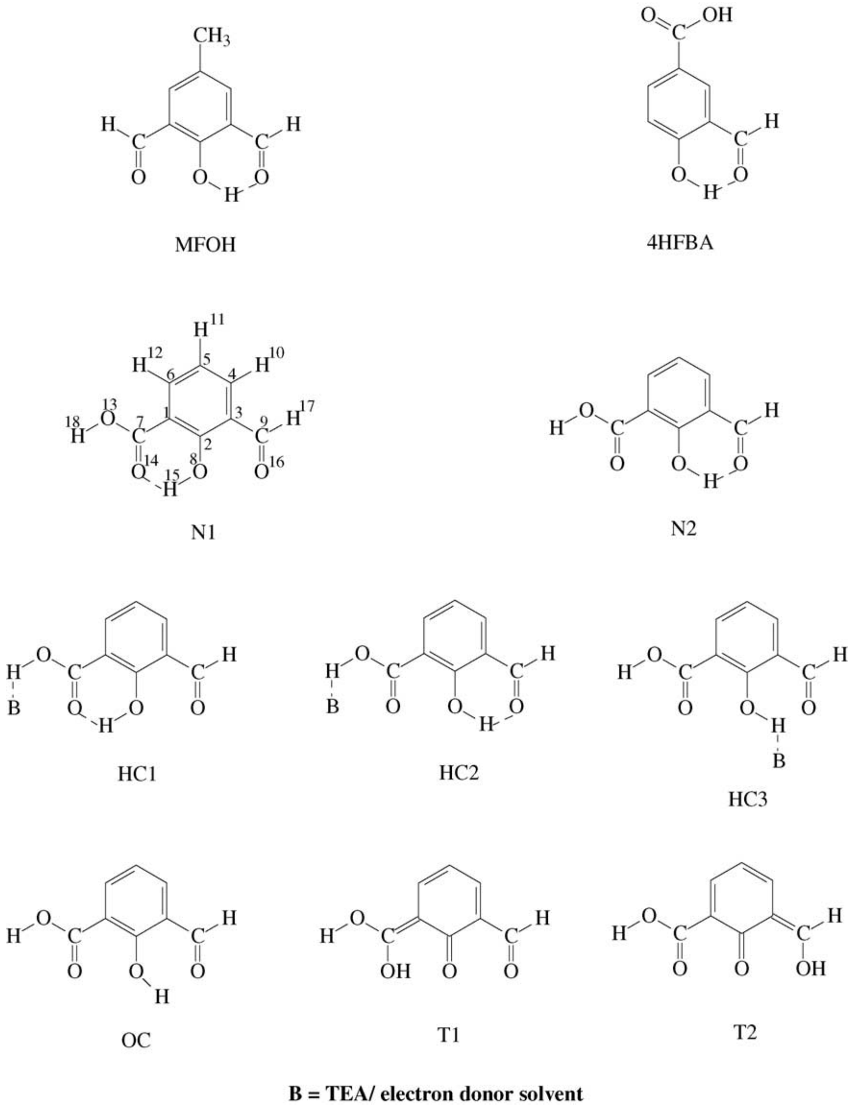


Fig. 2. The structural formulae of MFOH, 4HFBA and major species of 2HFBA present in the ground and excited state.

3.2. Emission spectra

The emission spectra of 2HFBA show a large Stokes shifted band (~10,500 cm^{-1}) at 505 nm in *n*-heptane and cyclohexane due to excited state intramolecular proton transfer (ESIPT) and formation of enol tautomer, T (T1, T2). On the addition of TEA, the tautomer band is shifted to 440 nm due to the rupture of the intramolecular bond and formation of HC3 type of hydrogen bonded complex (Fig. 3(b)). It is worth mentioning here that in the case of 4HFBA, the tautomer band remained almost unaffected by the added base. It is well established now that ESIPT can be observed only until the intramolecular bond exists in the molecule. Once the intramolecular bond is ruptured, ESIPT cannot be observed. In other words, one can say that the intramolecular bond in 2HFBA is ruptured by the added TEA and hydrogen bonded complex is formed. In the case of 4HFBA, TEA was unable

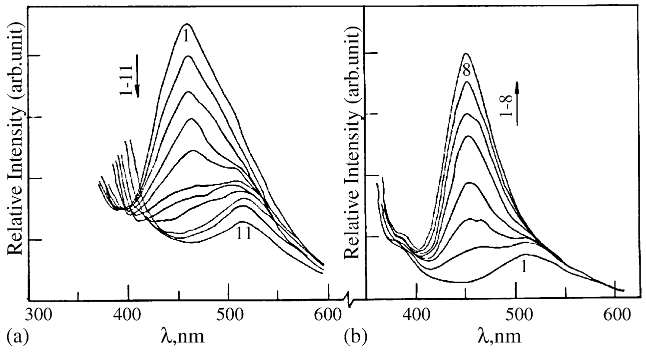


Fig. 3. λ_{exc} dependent emission spectra, (a) and emission spectra in presence of TEA, (b) in cyclohexane. Range of λ_{exc} (nm): 330 (1)–350 (11) and range of [TEA] = 0.0 (1)–9.2 × 10^{-5} (8) mol dm^{-3}.

to rupture the intramolecular bond. The emission spectra of 2HFBA in dioxane and THF show a single band at 440 nm. The emission spectra of 2HFBA in benzene show a strong band at 505 nm along with a shoulder around 440 nm. On the addition of TEA, the intensity of 440 nm band in dioxane and THF increases without any change in the position of the band while a single band appeared at 440 nm in benzene on addition of TEA. This 440 nm band can be attributed to the formation of hydrogen bonded complex, HC3 (open conformer), in the excited state. This observation shows that dioxane and THF are stronger electron donors than benzene inspite of the fact that benzene is a known π-donor. Relatively larger Stokes shift in the case of 4HFBA ($\sim$12,000 cm^{-1}) adds further support to the fact that intramolecular bond in 4HFBA is stronger than that in 2HFBA (Stokes shift $\sim$10,500 cm^{-1}). It is also observed in this study that on decreasing the λ_{exc}, the tautomer band gradually shifts to 450 nm in cyclohexane as shown in Fig. 3(a) i.e. OC-type open conformer is formed (Fig. 2). This indicates the presence of two species, even in pure non-polar solvents. In other words, selective excitation of either of the two forms is possible in non-polar solvent even in absence of base, in the case of 2HFBA. In the case of 4HFBA, the tautomer band was found to be independent of the excitation wavelength.

The excitation spectra of the tautomer emission (505 nm) shows a broad band peaking around 320–340 nm region as shown in Fig. 1(b) (6). This broad band indicates the presence of two species (N1 and N2, Fig. 2) in the ground state which may both be responsible for the tautomer emission. The excitation spectra of 440 nm emission show two bands at 315 and 340 nm in pure dioxane, whereas in presence of TEA, the excitation spectra of the 440 nm emission show a single band at 340 nm (Fig. 1(b)). None of the two excitation spectra (315 and 340 nm) agree with the corresponding absorption spectra. This indicates that the ground and excited state species in dioxane are different. The excited state species are formed after excitation and do not originate from the ground state species. The two bands in the excitation spectra of 440 nm emission indicate the presence of more than one species in the ground state.

Since the groups, –CHO, –COOH, and –OH lie adjacent to each other on the benzene ring, the phenolic proton can form intramolecular bond with the oxygen atoms of both the carboxyl and formyl groups. Although, the carboxylic and phenolic groups are both acids, the aromatic carboxylic acids exhibit a decrease in acidity in the first excited singlet state relative to the ground state. Phenols on the other hand, become stronger acids on excitation in the $\pi\pi^*$ singlet state and also *ortho–meta* directing towards substitution in the benzene ring [22]. Our theoretical calculations at AM1 level of approximation show that the total energy (ΔE_t) of the form, N1 is lower than that of N2 (Table 1) in the ground state. Hence, the form N1 is predicted to be more stable and hence more dominant than N2 in the ground state. This adds support to the fact that HC1 type hydrogen bonded complex formation is more probable than HC2 type complex in the ground state. However, the difference in the heats of formation of N1 and N2 is only 0.1 kcal/mol. Hence, conversion from one form to the other can take place easily. Details of the theoretical results have been discussed later. Our theoretical calculations also indicate that T2-type of tautomer is more stable than T1-type in the excited state (ΔE_t values of T1 and T2 are −2384.511 and −2384.810 eV, respectively). Accordingly, TEA will interact with the phenolic proton to form open conformer, HC3-type complex in the excited state (Fig. 2). Hence, it can be said that the hydrogen bonded complexes formed in the ground and excited states are different. In the case of dioxane and THF, the hydrogen bonded complex is formed even via interaction with electron donor solvents. On the addition of TEA, the intensity of 440 nm band increases due to the formation of more and more complex. In the case of MFOH, dual emission for enol tautomer and open conformer had been observed in dioxane and THF [1,2]. In the case of 4HFBA, the tautomer band was found to remain unaffected in benzene on addition of TEA. Scheme 1 (shown below) summarizes the possible reactions in case of 2HFBA.

Table 1
Selected ground state geometrical and energy parameters of 2HFBA in two of its limiting stationary points[a] (primary forms N1 and N2) in the S_0 state

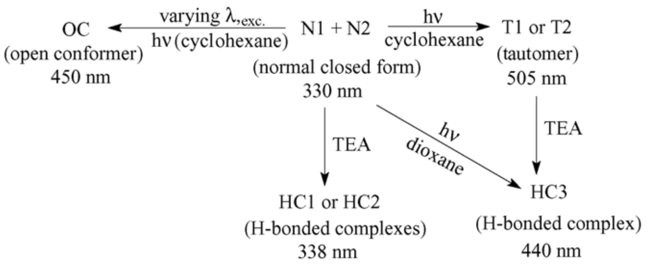
Parameter	N1	N2
ΔE_t (eV)	−2388.595	−2388.591
ΔH_f (kcal/mol)	−141.16	−141.06
C1—C2	1.415	1.421
C2—C3	1.420	1.414
C3—C9	1.471	1.465
C9—O16	1.230	1.236
H15· · ·O16	–	2.008
O14· · ·H15	2.017	–
O8—H15	0.975	0.974
C2—O8	1.357	1.357
C1—C7	1.461	1.465
C7—O14	1.241	1.233
C2—O8—H15	110.8	110.7
O8—C2—C3	115.7	124.5
C2—C3—C9	121.9	123.2
C3—C9—O16	125.0	124.4
C1—C2—O8	124.6	115.7
C2—C1—C7	121.1	120.2
C1—C7—O14	128.6	130.2
C1—C2—O8—H15	0.0	−180.0
O8—C2—C3—C9	0.0	0.0
C3—C2—O8—H15	−180.0	0.0
C2—C3—C9—O16	0.0	0.0
C7—C1—C2—O8	0.0	0.0
O14—C7—C1—C2	0.0	1.1
O14—C7—O13—H18	0.0	0.0

ΔE_t and ΔH_f stand for total energy and heat of formation respectively.

[a] Bond lengths are in angstroms and angles are in degrees.

4. Low temperature emission spectra of 2HFBA at 77 K

The low temperature emission and excitation spectra of 2HFBA are shown in Fig. 4. Unlike 4HFBA, 2HFBA shows



Scheme 1.

phosphorescence on irradiation even in pure *n*-hexane on lowering the temperature to 77 K. 4HFBA showed phosphorescence only in presence of a base in non-polar solvents [4]. On the other hand, emission spectra of MFOH at 77 K consisted of a Stokes shifted fluorescence and phosphorescence spectra in *n*-hexane [1]. It has been shown earlier [1,15,16] that appearance of phosphorescence is from open conformer and due to the rotation of formyl group. For the formation of open conformer, rupture of the intramolecular bond is necessary. Our observation shows that intramolecular bond in 2HFBA has been ruptured on lowering the temperature to 77 K even in pure non-polar solvent. The low temperature fluorescence excitation spectra as well as phosphorescence excitation spectra occur at 330 nm which agrees with the absorption spectra of the normal closed form. Accordingly, it can be said that the main species present at this low temperature before irradiation is the normal closed form. Also, no change has been observed in the fluorescence and phosphorescence spectra with the variation in excitation wavelength at 77 K. On the other hand, in the case of 4HFBA, pure non-polar solvent was unable to rupture the intramolecular bond even on lowering the temperature to 77 K. This adds further support to the fact that the intramolecular bond in 4HFBA is stronger than that in 2HFBA.

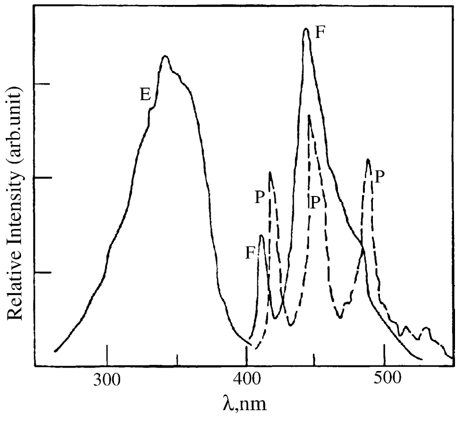


Fig. 4. Fluorescence (F), phosphorescence (P) and phosphorescence excitation (E) spectra of 2HFBA in *n*-hexane at 77 K. Shutter control corrected spectra. $\lambda_{exc} = 330$ nm.

5. Molecular structure and energetics of proton transfer in S_0 and S_1 electronic states of 2HFBA

Often the theoretical results serve as an essential feedback to explain the experimental observations. Rovira and Scheiner [23] identified a clear relationship between the intramolecular hydrogen bond strength and barrier to proton transfer. It was also suggested that the higher barrier is associated with the weaker hydrogen bond strength.

Using semi-empirical molecular orbital methods one can often make predictions about the relative stabilities of similar compounds, construct reaction paths and potential energy surfaces fairly successfully. In this paper, we have tried to do some theoretical investigation on the proton transfer reaction of 2HFBA in a semi-empirical framework at the AM1 level of approximation.

5.1. S_0 electronic state

Table 1 shows the optimized equilibrium geometrical and energy parameters of 2HFBA in its two normal closed forms obtained semi-empirically at the AM1 level of approximation. The atom numbering are given in Fig. 2. It can be seen from Table 1 that AM1 calculation predicts a planar geometry with considerable hydrogen bonding [distances, O14· · ·H15 = 2.017 Å for N1 and H15· · ·O16 = 2.008 Å for N2]. The difference in the determined intramolecular bond distance between the forms, N1 and N2 is only ±0.009 Å. In other words, intramolecular bond strengths are almost same for the two cases. Also, the difference in the heats of formation between the forms, N1 and N2 is only 0.1 kcal/mol. The geometrical parameters of the aromatic ring do not differ significantly for N1 and N2. This is also true for the total energy values (ΔE_t) of N1 and N2 (Table 1). It is also observed that the activation energy required for dihedral angle (C1-C2-O8-H15) rotation from N1 to N2 is only 4.86 kcal/mol and occurs at a value of 92.9°. In this regard, we would like to state that the computed barrier heights are generally a bit overestimated at the AM1 level of approximation so that the actual barrier height might be somewhat smaller. Accordingly, flipping over from N1 to N2 is easily possible in the ground state. Also, the ΔE_t values obtained for the hydrogen bonded complexes, HC1 and HC2 (Fig. 2) are −3571.008 and −3570.992 eV, respectively indicating that HC1 dominates over HC2 in the ground state.

In Table 2, we have shown the optimized equilibrium geometrical and energy parameters characterizing the proton transfer in 2HFBA in the S_0 state at the AM1 level of approximation. The changes in the bonding pattern observed around the chelate ring (HOCCCO) are quite significant. In the benzene ring of the primary form, all the C–C bond lengths are predicted to be nearly equal, showing the delocalisation of the π orbitals over the entire ring. However, in the tautomeric form, C1–C6 and C4–C5 bond lengths decrease significantly while the others increase. This indicates that ring current delocalisation is partially lost following the proton transfer.

Table 2
Selected geometrical and energy parameters of 2HFBA in two of its limiting stationary points[a] (N2 and T2) in the S_0 state

Parameter	Primary	Tautomer
ΔE_t (eV)	−2388.591	−2388.028
ΔH_f (kcal/mol)	−141.06	−128.08
C3—C9	1.465	1.371
C1—C6	1.396	1.360
C1—C2	1.421	1.470
C2—C3	1.462	1.473
C3—C4	1.404	1.414
C4—C5	1.388	1.355
C5—C6	1.396	1.434
C9—O16	1.236	1.340
H15—O16	2.008	0.980
O8—H15	0.974	1.976
C2—O8	1.357	1.246
C2—C3—C9	123.2	122.0
C3—C9—O16	124.4	127.8
C3—C2—O8	124.5	121.1
C2—O8—H15	110.7	–
C9—O16—H15	–	112.2
O8—C2—C3—C9	0.0	−4.2
C3—C2—O8—H15	0.0	–
C2—C3—C9—O16	0.0	0.0
C3—C9—O16—H15	–	−0.3

[a] Bond lengths are in angstroms and angles are in degrees.

Table 3
Energy parameters of the transition state of 2HFBA: TS1, lying between the primary closed forms N1 and N2, in the S_0 state; TS2 and TS3 characterizing the tautomerization, N2 to T2 in the S_0 and S_1 states, respectively

Parameter	TS1	TS2	TS3
ΔE_t (eV)	−2388.384	−2387.454	−2384.137
ΔH_f (kcal/mol)	−136.30	−114.83	−38.36

The corresponding parameters for the primary forms N1 and N2 are reported in Table 1. The corresponding parameters for the normal and tautomeric forms (N2 and T2) are reported in Tables 2 and 5.

Table 3 reports some of the relevant data for the energy parameters of the transition state (TS) that characterizes the proton transfer pathway of 2HFBA in the S_0 and S_1 states. The activation barrier is quite high in the S_0 state so that proton transfer rate is expected to be very low (Table 4). This corroborates our experimental observation that proton transfer does not take place in the S_0 state of 2HFBA at all [1].

5.2. *S_1 electronic state*

Table 5 shows the optimized geometry of all the relevant stationary points along with their energetics during the proton transfer in the S_1 electronic state of 2HFBA. The important point to note here is that the tautomerization energy for the enolic form is predicted to be −9.09 kcal/mol (Table 4). Thus, the endothermic proton transfer process in the S_0 state is predicted to become an exothermic one in the S_1 state. Comparing the geometrical parameters of 2HFBA in the S_0 (primary) and S_1 (tautomer) states, one can see that drastic changes have occurred in the hydrogen bonded chelate ring (Tables 2 and 5). The C2–O8 single bond in the primary form has been converted to a double bond similar to the C3–C9 bond. The C9–O16 double bond of the carbonyl moiety has been converted to a single bond. Accordingly, the phenolic structure in the ground state is converted to an enol like structure upon $S_1 \leftarrow S_0$ excitation, which is consistent with our experimental results.

Table 4
Energetics of tautomerization of 2HFBA in S_0 and S_1 states

Parameter	S_0	S_1
ΔE_{taut} (kcal/mol) (tautomerization energy)	12.98	−9.09
ΔE_{act} (kcal/mol) (activation energy)	26.23	6.47

Table 5
Selected geometrical and energy parameters of 2HFBA in two of its limiting stationary points[a] (N2 and T2) in the S_1 state

Parameter	Primary	Tautomer
ΔE_t (eV)	−2384.416	−2384.810
ΔH_f (kcal/mol)	−44.82	−53.91
C3—C9	1.438	1.422
C1—C6	1.396	1.429
C1—C2	1.427	1.420
C2—C3	1.462	1.473
C3—C4	1.392	1.372
C4—C5	1.402	1.444
C5—C6	1.406	1.361
C9—O16	1.250	1.324
H15—O16	1.888	0.984
O8—H15	0.987	1.879
C2—O8	1.330	1.266
C2—C3—C9	121.8	120.0
C3—C9—O16	123.9	127.0
C3—C2—O8	122.2	119.8
C2—O8—H15	111.9	–
C9—O16—H15	–	112.4
O8—C2—C3—C9	3.5	−3.6
C3—C2—O8—H15	−2.7	–
C2—C3—C9—O16	−0.4	1.9
C3—C9—O16—H15	–	0.9

[a] Bond lengths are in angstroms and angles are in degrees.

5.3. *Proton transfer mechanism and reaction path analysis*

To construct the reaction path representing the proton transfer in 2HFBA, O8–H15 distance (R) has been chosen as the coordinate. As the proton translocation distance of the mobile hydrogen atom is considered to be a key parameter for the construction of the ESIPT potential [24], the O8–H15 distance is varied between the primary and the equilibrium tautomeric O8–H15 distance. At each point, all geometrical parameters are fully optimized and the total energy (ΔE_t) is plotted against R. Interpolation through cubic spline is used to construct the potential energy curves representing the proton transfer process.

Fig. 5(a)–(c) shows the potential energy (PE) curves for the variation of total energy with R in the S_0 and S_1 states and also the variation of total energy with dihedral angle rotation,

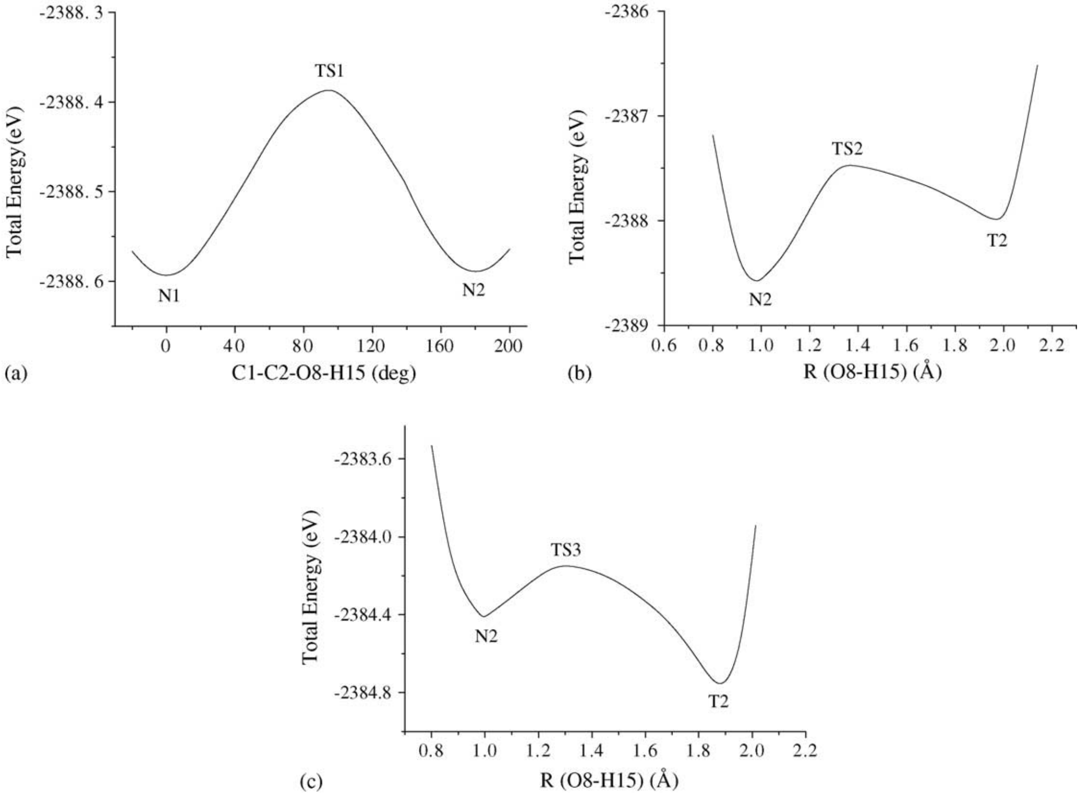


Fig. 5. (a) Variation of total energy as a function of the dihedral angle, C1—C2—O8—H15 in the S_0 state. Variation of total energy during the proton transfer in the S_0 state (b) and in the S_1 state (c).

i.e. conversion of the form N1 to N2 in the S_0 state. All the PE curves show two distinct minima. The minima in (b) and (c) indicate the corresponding primary and tautomeric forms, N2 and T2 in the S_0 and S_1 states, respectively while those in (a) indicate the two primary closed forms N1 and N2 in the S_0 state. In each case, the PE curve passes through a maximum which is the saddle point (SP) on the proton transfer path as confirmed by the diagonalization of the relevant force constant matrix at the particular point.

The maximum in the S_0 state is a true saddle point on the potential energy surface (PES) and occurs at a proton transfer distance of 1.31 Å, and that in the S_1 state at 1.17 Å. Table 4 denotes the exo(endo)thermicities (ΔE_{taut}) and activation energies (ΔE_{act}) for the tautomerization process of 2HFBA in the S_0 and S_1 states. It appears that the reaction is appreciably endothermic in the S_0 state. The activation energy for proton transfer is also quite high in the S_0 state. Hence, proton transfer in this state is unlikely. On the other hand, proton transfer reaction is predicted to be exothermic in the S_1 state. A relatively small proton transfer barrier in the S_1 state is indicative of a rather relatively shallow well characterizing the primary form. It may not be deep enough to contain an appreciable number of bound vibrational levels, so that the potential is effectively of the anharmonic single well type. From the nature of the S_0 and S_1 surfaces (Fig. 5(b) and (c)), it appears that in the excited S_1 state, the vibrational excitation would take the system almost over the barrier and eventually into the potential well representing the tautomeric form. This is the reason why we have observed the tautomer emission from the S_1 state. However, this does not necessarily mean that the S_1 surface is a single well potential. We may therefore conclude that the proton transfer in the S_1 state may be a vibrationally assisted over-barrier process at room temperature.

6. Conclusion

In the case of 2HFBA, different kinds of hydrogen bonded complex and tautomer have been observed due to the presence of both formyl and carboxyl groups close to the phenolic group and due to flipping between them. Our results show that the magnitude of the Stokes shift and the strength of intramolecular bond have decreased significantly in the case of 2HFBA compared to 4HFBA due to the change in the position of −COOH group in benzene ring. Unlike 4HFBA, 2HFBA shows ESIPT only in pure non-polar solvent while phosphorescence is observed even in absence of base in non-polar solvents.

An interesting observation of this present work is that the intramolecular bond has been seen to rupture even in pure non-polar solvent, simply on changing the λ_{exc}. The AM1 calculations on S_0 and S_1 states of 2HFBA show that the proton transfer process is thermodynamically endothermic in the ground state and also encounters high activation barrier. In the S_1 state, the process become exothermic with a relatively low barrier.

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