The tautomer ground state could not be trapped at low absorptions, which has stimulated hope to find an intrinsic barrier to states and the first excited singlet states of the normal form and observations. In particular, the observation of long-lived transient absorptions has led to the experimental solution phase spectra of Figure 9. A slight broadening with increasing temperature leads to a decrease in the maximum molar absorptivity with temperature. The calculated molar absorptivity at 440 nm varies from 8940 to 5280 M⁻¹ cm⁻¹ on going from 5 to 35 °C.

The spectrum calculated at 77 K, shown in Figure 8, is considerably sharper than the room temperature spectrum, in agreement with experiments on related systems. The calculated molar absorptivities at 356 and 440 nm are 7414 and 9270 M⁻¹ cm⁻¹, respectively.

Conclusions

In this work we have explored the orientation dependence of spectroscopic electron transfer in the indene-TCNE EDA complex. By calculating the energy and CT spectra as a function of complex geometry, it has been shown that the first and second charge-transfer transitions are allowed in a wide range of energetically accessible conformations. Investigation of the ground-state intermolecular potential also shows that fairly small energy barriers of the order of kT at room temperature separate the minima associated with possible orientational and translational isomers. Thus, for indene–TCNE, there is no correspondence between the two CT bands and distinct complex geometries.

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AM1 and INDO/S Calculations on Electronic Singlet and Triplet States Involved in Excited-State Intramolecular Proton Transfer of 3-Hydroxyflavone

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Energies and geometries of the electronic ground states and vertical transition energies and oscillator strengths of singlet–singlet and triplet–triplet transitions have been calculated for both tautomer forms of 3-hydroxyflavone. The resulting energy level diagram and calculated excited-state spectra yield a consistent interpretation of the data from transient absorption measurements. It is concluded that all long-lived transient absorptions are due to triplet species and that an intrinsic barrier to proton transfer exists in the lowest triplet state.

Introduction

Among the molecules which display an excited-state intramolecular proton transfer (ESIPT) reaction, 3-hydroxyflavone (3-HF) is one of the most extensively studied. However, as more and more experimental information on this system is collected, it appears that a simple four-level picture involving the ground states and the first excited singlet states of the normal form and the tautomer form of this molecule cannot explain all the observations. In particular, the observation of long-lived transient absorptions has stimulated hope to find an intrinsic barrier to the backward (ground-state) intramolecular-proton-transfer reaction, but the tautomer ground state could not be trapped at low temperatures.


An impediment to the interpretation of the experimental data is the fact that the relative ordering of the singlet and triplet states of both tautomer forms of 3-HF is not known. Bouman et al. have performed ab initio calculations on the ground state and the first σπ* excited state of 3-HF, but calculations on other states do not yet exist. This paper presents results of semiempirical molecular-orbital calculations for several singlet and triplet levels of both tautomer forms of 3-HF. For the triplet manifold of the zwitterionic tautomer these calculations predict rather unusual properties which yield a consistent interpretation of the experimental data available so far.

These experimental findings will be briefly summarized in the following. We denote the singlet and triplet states of the normal form of the molecule by the symbols Sₐ and Tₐ and the corresponding states of the tautomer form by S₄ and T₄. (In other molecules these forms are often termed enol and keto forms. In 3-HF, however, proton transfer changes the enol form to a...

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zwitterionic enolate structure for which no electrically neutral keto structure can be drawn.

Excitation of the normal form of 3-HF leads to the first excited singlet state $S_1$ of $a^*g^*$ character. The first maximum of this transition occurs at 30 800 cm$^{-1}$ in the gas phase at 478 K and at 28 400 cm$^{-1}$ in alkane solution at room temperature. The extinction coefficient is $1.7 \times 10^4$ M$^{-1}$ cm$^{-1}$ at the maximum of the first absorption band at 29 200 cm$^{-1}$. Via rapid proton transfer $S_1 \rightarrow S_1'$ population is transferred to the first excited singlet state of the tautomer. The fluorescence $S_1' \rightarrow S_0'$ of this species in alkane solutions peaks at $\lambda = 526$ nm (19 000 cm$^{-1}$) with a quantum yield of 0.36 and a decay time of 3 ns at room temperature in methycyclohexane (MCH). Other papers report a decay time of 3 ns in benzene, $4 \text{ ns}$ in cyclohexane, and $4.6 \text{ ns}$ in MCH. When the molecule is isolated in an argon matrix at a temperature of 15 K, the ESIPT reaction is still very fast with a lifetime of $1.3 \text{ ps}$ for the uncomplexed molecule. Like alcohols and ethers are not quenched by oxygen with a slightly higher bimolecular rate constant than in benzene. $\text{O}_2$ quenching of this process was deaerated. When the sample was deaerated, it is quenched by oxygen with a slightly higher bimolecular rate constant than in benzene. $\text{O}_2$ quenching of this process was $1.4 \text{ ns}$ in aerated solution, and with a quantum yield of only 0.013.

On the basis of the calculations discussed below, the first transient absorption is assigned to $T_1 \rightarrow T_0$ transitions and the second transient absorption to $T_1' \rightarrow T_0'$ transitions. The first assignment is in complete agreement with that given in the experimental papers. The second transient species has been previously assigned to the tautomer ground state. Brewer et al. also considered a possible assignment of this transient species to the tautomer triplet state. To explain the results of the two-step laser excitation (TSLE) experiments, they proposed a decay mechanism involving a reverse intersystem crossing (ISC) step, $T_1' \rightarrow S_0'$, and another step not hindered by an intrinsic barrier. The decay time of the tautomer fluorescence increases to 8 ns under these conditions. The origin of the $S_0' \rightarrow S_1'$ transition of the isolated molecule in a supersonic jet has a Lorentzian line shape with a homogeneous line width of 4.1 cm$^{-1}$, which may be interpreted in terms of a lifetime of 1.3 ps for the $S_1$ state.

Transient absorption measurements of 3-HF in hydrocarbon solvents have been performed in the picosecond and microsecond time domain. (Investigations performed with 3-HF in hydrogen-bonding solvents like alcohols and ethers are not considered here, since the hydrogen-bonded complexes of 3-HF with solvent molecules behave distinctly differently from the uncomplexed molecule.) Immediately after excitation, gain transient absorption at 22 700 cm$^{-1}$ with 4 ns decay time has been reported in ref 10. Two transient absorptions with decay times of several microseconds have been observed in non-hydrogen-bonding solvents. The first has a peak at 395 nm (25 300 cm$^{-1}$) and decays with a time constant of 7.2 ps. It is quenched by oxygen with a bimolecular rate constant of $2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and singlet oxygen is formed. The second transient absorption peaks at 17 70 nm (22 900 cm$^{-1}$) and decays with a time constant of 14.2 ps. It is also quenched by oxygen with a slightly higher bimolecular rate constant of $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (in ref 2 the decay time of this transient was reported to be $2.9 \text{ ps}$ in aerated solution, which did not change much upon passing a stream of nitrogen through the sample. However, the same group found that in benzene solution the lifetime of this transient increases from 5.9 to 14.5 ns when the sample was deaerated.) Excitation of this transient species with a second light pulse results in fluorescence from the tautomer, $S_1' \rightarrow S_0'$, but with a quantum yield of only 0.013.


Figure 1. Bond lengths (in angstroms) and bond angles (in degrees) for the electronic ground states of 3-hydroxyflavone: (top) X-ray structure of the normal form, (middle) AM1 optimized geometry of the normal form, (bottom) AM1 optimized geometry of the tautomer form.

The root-mean-square deviation for the bond lengths between non-hydrogen atoms is 0.016 Å. It should be kept in mind that the AM1 method has been optimized to reproduce geometries of isolated molecules. The crystal packing might lead to systematically smaller bond lengths. The calculated dihedral angle between the phenyl ring and the hydroxycromone part is 29.2°; the experimental value is 5.5°. It is known that the intermolecular forces in the crystal can strongly reduce dihedral angles of this kind. For example, the molecule biphenyl has a planar structure in the crystal, whereas the dihedral angle is ≈45° in the vapor phase. The calculated dihedral angle of 29.2° is thus reasonable for the 3-HF molecule in solution. (It should be mentioned that much larger deviations from the experimental geometry are found with the MNDO method in its original parametrization. In this case a dihedral angle of almost 90° between both molecular parts is calculated.)

The calculated geometry of the S₁ state shows that the whole molecular frame is rearranged upon intramolecular proton transfer. The largest change occurs for the C–O bonds of the keto and the hydroxy group. After proton transfer the C₁–O bond shrinks by 0.115 Å, whereas the C₆–O bond length increases by 0.114 Å. (See Figure 2 for the numbering of the atoms.) The single- and double-bond characters of these two bonds are thus reversed. The double-bond character of the C₃–C₄ bond is strongly reduced, and that of the C₃–C₈ bond strongly increases. The C–O bond lengths of the ether group become slightly shorter, and the anellated benzene ring exhibits a small tendency toward localization of the double bonds at the C₅–C₆ and C₇–C₈ bonds. All these observations could be interpreted as arising from an admixture of the resonance structures c and d in Figure 2. Whereas the bond lengths and angles in the phenyl ring show almost no change due to proton transfer, the bond connecting it to the 3-hydroxychromone becomes slightly shorter and the dihedral angle reduces to 14.1°, indicating an increase of the conjugative interaction between both parts of the molecule.

Excited States and Spectra. The energy level diagram of the calculated singlet and triplet states of the two tautomeric forms of 3-HF is shown in Figure 3. The vertical arrows indicate radiative transitions, and the numbers are calculated oscillator strengths. The intramolecular-proton-transfer reaction is initiated by excitation of the normal form of 3-HF to its first excited singlet state S₁. In the calculation based on the AM1 geometry the S₁ state is of π* character, whereas the experimental extinction coefficient indicates ππ* character for this state. The calculated singlet and triplet states of the normal form of 3-HF (left) and its tautomer form (right). Vertical arrows indicate radiative transitions, and the numbers are calculated oscillator strengths. The left energy scale refers to the heat of formation of the AM1 method; the right scale is relative to the electronic ground state S₀.

Figure 2. Numbering scheme of atoms in 3-hydroxyflavone in its normal form (a) and some resonance structures of the tautomer form (b–d).

Figure 3. Energy level diagram of the calculated singlet and triplet states of the normal form of 3-HF (left) and its tautomer form (right). Vertical arrows indicate radiative transitions, and the numbers are calculated oscillator strengths. The left energy scale refers to the heat of formation of the AM1 method; the right scale is relative to the electronic ground state S₀.

observed maximum at 19 000 cm⁻¹. The strongest transitions of cm⁻¹. The transient absorption with 44s decay time observed spectral range which already strongly overlaps with the absorption transferred to SI'. The transient absorption spectrum calculated to have low oscillator strengths, except the reverse of the gain profile.9 It is concluded that proton transfer back to the transient absorption measurements have been performed in this ps.10 Finally, even at temperatures below 15 K the tautomer transient absorption could be seen with a time resolution of 30 ps.10 Evenly, at temperatures below 15 K the tautomer ground state could not be trapped in argon matrices.12,22 Hence, the back-reaction S₀ → S₀ cannot be a thermally activated process and should be very fast at room temperature. It is, therefore, extremely unlikely that the transient species with ~14-μs decay time observed in refs 3 and 4 is the tautomer ground state S₀.

The possibility should thus be examined that both long-lived transient absorptions are due to triplet species. The most likely candidates are T₁ and T₁'. The experimental papers agree in the assignment of the transient species with absorption peak at 25 300 cm⁻¹ and 7.2-μs decay time to a triplet state. The choice of T₁ however, should be reexamined since it was mainly based on the assignment of the other species to the tautomer ground state. The calculated absorption spectrum of T₁ has three reasonably intense transitions in the near-UV region: T₁ → T₁₈ (28 900 cm⁻¹, f = 0.050), T₁ → T₁₅ (29 400 cm⁻¹, f = 0.131), and T₁ → T₁₂ (30 100 cm⁻¹, f = 0.11). The strongest low-lying transitions starting from T₁' occur at lower energies, namely, T₁' → T₁': (16 700 cm⁻¹, f = 0.039), T₁' → T₁' (25 900 cm⁻¹, f = 0.104), and T₁' → T₁₀ (27 400 cm⁻¹, f = 0.139). The relative magnitude of the transition energies suggests to assign the transient absorption at 25 300 cm⁻¹ to the T₁ state and the first excited singlet state. These shifts are not known individually, and we assume that they are similar in size. This is in line with the calculated energy values and with the experimental observation that the proton-transfer reactions in both states are irreversible.

The gap between S₀ and S₀' is calculated to be rather small, namely, 5800 cm⁻¹. This energy is only slightly smaller than the amount needed to produce singlet oxygen in an oxygen quenching reaction. The calculated energy gap between T₁ and S₀ of 19 000 cm⁻¹ is sufficiently large for the production of singlet oxygen. The phosphorescence T₁ → S₀ should occur in the visible spectral range and might be observable at low temperatures.

Discussion

The assignments made in the preceding section have important consequences for the photophysics of 3-HF. These will be discussed in the following based on the level diagram shown in Figure 4 which has been composed to agree with the experimentally known as well as the calculated energy data, keeping in mind that the latter are only accurate to within ±2000 cm⁻¹. The experimental S₀ → S₁ excitation energy is ~27 500 cm⁻¹; that of the fluorescence transition S₁ → S₀ is ~19 500 cm⁻¹. The Stokes shift of ~8000 cm⁻¹ is the sum of the energy shifts of the ground state and the first excited singlet state. These shifts are not known individually, and we assume that they are similar in size. This is in line with the calculated energy values and with the experimental observation that the proton-transfer reactions in both states are irreversible.

The gap between S₀' and T₁' in Figure 4 is ~8000 cm⁻¹, slightly larger than the calculated value of 5800 cm⁻¹. This accounts for the fact that quenching of T₁' with oxygen produces singlet oxygen, since the observed quantum yield of photooxidation products is very low.4 If the gap between T₁' and S₀' were too small to provide the energy needed for the production of singlet oxygen, a quenching reaction T₁' → S₀ would have to be postulated. Such a process involving simultaneous ISC and proton transfer seems to be rather unlikely.

If we assume that T₁ is slightly lower than calculated, it will be almost isoenergetic with T₁'. In this case a barrier to ESIP onto the lowest triplet surface could exist. Such a situation has been previously observed in the molecule 2-(2-hydroxyphenyl)benzoxazole.34 A barrier must be postulated to account for the long 

Figure 4. Energy level diagram of the lowest electronic states of the normal form of 3-HF (left) and its tautomer form (right). The various photophysical processes are indicated by straight arrows (radiative transitions), curved arrows (proton transfer), broken arrows (ISC), and dotted arrows (IC).
lifetime of both triplet states. If we assume that the decay of $T_1$ is mainly due to proton transfer, the decay time of $7.2$ $\mu$s at room temperature corresponds to an energy barrier between 39 and 50 $k_B T$ for a reaction with a frequency factor between $10^{12}$ and $10^{14}$ s$^{-1}$. To check this prediction, we propose to populate $T_1$ with a triplet sensitizer. In this case $T_1'$ should not initially be populated, and the transient absorption at 22 900 cm$^{-1}$ should grow in with the decay time of $T_1$.

A question that remains to be answered concerns the pathway of population of $T_1$ after excitation of 3-HF to the $S_0$ state. The direct way would be ISC $S_1 \rightarrow T_1$. In this case ISC must be very fast to compete with ESIP. Fast ISC on a picosecond time scale has indeed been observed for several aromatic ketones, but it is questionable whether these processes are really fast enough to compete with ESIP. Alternatively, $T_1$ could be populated through ISC combined with reverse proton transfer, $S_1' \rightarrow T_1$. The probability of such a simultaneous process should, however, be rather low. An interesting decay path involves the $T_1$ surface. According to the calculations, $T_1'$ is slightly above $S_1'$, but the reversed ordering is also in accordance with the accuracy of the calculations. Hence, $T_1'$ could be populated via ISC from $S_1'$. The calculations also predict that $T_1$ is below $T_1'$; thus, proton back-transfer should occur on the $T_1$ surface. Subsequent internal conversion (IC) $T_1 \rightarrow T_1$ then leads to population in $T_1$. If $T_1$ is mainly populated by direct ISC, the transient absorption at 25 300 cm$^{-1}$ should rise with the same rise time as the tautomer fluorescence. For the two other processes the bottleneck will be $S_1'$, and the transient absorption should rise with the same rise time of the tautomer fluorescence. If the path involving the $T_1$ state is active, excitation of $T_1'$ should lead to an increase of the transient absorption assigned to $T_1$.

The large energy gap between $T_1'$ and $T_1'$ has important consequences for the explanation of the two-step laser excitation (TSLE) experiments. Excitation $T_1' \rightarrow T_1'$ will, after IC $T_1' \rightarrow T_1'$, lead to population in $T_1'$. This population can decay in three ways: internal conversion $T_1' \rightarrow T_1'$, reverse proton transfer $T_1' \rightarrow T_2$, and reverse ISC $T_1' \rightarrow S_1'$. Internal conversion should be slow due to the large energy gap. The reverse proton transfer has been discussed above as a possible path for the population of $T_1$. The molecules produced in $S_1'$ via reverse ISC will lead to the typical tautomer fluorescence $S_1' \rightarrow S_0'$. The apparent quantum yield of tautomer fluorescence following excitation of the 14.2-$\mu$s species was estimated to be 0.013 in ref 4, compared to 0.36 for the population of $S_1'$ via proton transfer. If the latter value is interpreted as the intrinsic quantum yield of tautomer fluorescence at room temperature, an estimated yield of 0.036 is calculated for reverse ISC $T_1' \rightarrow S_1'$. A large yield of reverse ISC has previously been found for other molecules with a large energy gap between $T_1$ and $T_2$. In 9-phenylanthracene (9-PA) and 9-methylanthracene (9-MA) these yields are $8.3 \times 10^8$ and $6.1 \times 10^8$.

The rate constant for the reverse ISC is $4.9 \times 10^6$ s$^{-1}$ in 9,10-dihydroanthracene an even larger yield of 0.19 has been found. The energy gap between $T_1$ and $T_2$ is $-11000$ cm$^{-1}$ in these molecules. In 3-HF the gap is probably larger, leading to an even slower decay of $T_2$ through internal conversion. The presence of a keto group might further speed up the reverse ISC. But the dominant decay process of $T_2'$ might well be the reverse proton transfer.

An order-of-magnitude estimate of the rate constants involved in the decays of the states $S_1'$ and $T_1'$ can be based on the following arguments. Let us denote the rate constants of forward and backward ISC between $S_1'$ and $T_1'$ by $k_{TS}$ and $k_{ST}$ and the rate constants of the decays of $S_1'$ and $T_1'$ to other states by $k_a$ and $k_f$, respectively. The ratio of the two ISC rate constants depends on the energy difference $\Delta E = E(T_1') - E(S_1')$, through

$$k_{ST} = \frac{1}{\exp \left( \frac{\Delta E}{k_B T} \right)}$$

(1)

The ratio of the quantum yield of TSLE fluorescence and the normally excited tautomer fluorescence within this model is

$$\frac{\Phi_{F, TSLE}}{\Phi_F} = \frac{k_{TS}}{k_{TS} + k_T}$$

(2)

The experimental value of this ratio is 0.036, leading to $k_{TS}/k_T = 26.8$. Thus, the decay of $T_2'$ to $T_1'$ and $T_2$ is much faster than reverse ISC. Hence, the total decay rate constant of $S_1'$ is in good approximation given by the sum of $k_a$ and $k_f$. Its value at room temperature is $2.5 \times 10^8$ s$^{-1}$.

If we assume that the main contribution to $k_f$ is the radiative decay with a quantum yield of 0.36, a value of $1.6 \times 10^8$ s$^{-1}$ is found for $k_{TS}$. If $S_1'$ and $T_1'$ are isoenergetic, eq 1 leads to $k_{TS} = 5.3 \times 10^8$ s$^{-1}$. Equation 2 then yields $k_T = 1.4 \times 10^8$ s$^{-1}$, corresponding to a lifetime of 700 ps for $T_1'$. With $\Delta E = 500$ cm$^{-1}$ one obtains $k_{TS} = 6.0 \times 10^8$ s$^{-1}$, $k_T = 1.6 \times 10^9$ s$^{-1}$, and a lifetime of $T_1'$ of 62 ps.

The relative ordering of the states $S_1'$ and $T_1'$ could experimentally be verified through measurement of the temperature dependence of the yield of $T_1$ after normal excitation and the yield of reverse ISC after two-step laser excitation. If $T_1'$ is slightly higher than $S_1'$ as suggested by the calculations, the forward ISC step would be thermally activated. With decreasing temperature the decay of $S_1'$ through this channel should become slower, leading to a lower quantum yield of $T_1$ and a longer lifetime of $S_1'$. The latter fact is indeed observed but could also be due to a different thermally activated radiationless decay channel. If $T_1'$ is below $S_1'$, the reverse ISC step should be thermally activated. Then the apparent quantum yield of tautomer fluorescence after TSLE relative to that after direct excitation should decrease with decreasing temperature.

Conclusions

The comparison of our calculations with the experimental data known from the literature leads us to the following conclusions:

1. The two long-lived transient species with decay times of 7.2 and 14.2 $\mu$s are assigned to the states $T_1$ and $T_1'$.

2. As a consequence of this assignment, a substantial barrier to proton transfer must exist along the potential curve of the lowest triplet state.

3. An unusually long lifetime of several picoseconds is proposed for the second excited triplet state $T_2'$ of the tautomer. This fact allows ISC to the $S_1'$ state to compete with the decay of $T_2'$ to $T_1'$ and reverse proton transfer to $T_1'$. The transition $T_2' \rightarrow T_1'$ could also lead to an observable triplet–triplet fluorescence.

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