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Ab Initio Study of Ground and Excited State Proton Transfer in 2-(2'-Hydroxyphenyl)benzoxazole

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The structures, hydrogen bonding, intramolecular proton transfer processes, and vibrational frequencies of 2-(2'-hydroxyphenyl)benzoxazole in the ground state and the first excited singlet state were investigated by *ab initio* calculations (mainly at the SCF and CIS 3-21G* levels, but with supplementary calculations at the SCF/6-31G*, MP2/3-21G*, and MP3/3-21G* levels). Analysis of intramolecular proton transfer included plots of energy, O··N distance, and O··H distance as functions of the internal reaction coordinate. The results confirm that the most stable forms are the (O−H·· ·N)-bonded enol form in the ground state and the (O· · ·H−N)-bonded keto form in the first excited singlest state and suggest an in-plane mechanism for the excited state proton transfer which is powered by the O−H stretching vibration once the O and N atoms have been brought into proximity by in-plane bending.

Introduction

The chemical and biochemical importance of proton transfer reactions has long been recognized.[1] This general interest along with their role in chemiosmosis[2] amply justifies research on their mechanisms and structural requisites.[3] However, even for intramolecular processes the number of molecules whose structures have been investigated experimentally during proton transfer is insufficient to allow systematic conclusions to be drawn; experimental characterization of intermolecular proton transfer structures is even more difficult. In these circumstances, theoretical studies of these processes are of particular importance.

Many molecules with intramolecular hydrogen bonds undergo intramolecular proton transfer in the excited state (ESIPT). Heteroaromatic molecules exhibiting ESIPT have been reviewed by Barbara *et al.*[4] They include 2-(2'-hydroxyphenyl)benzoxazole (HBO),[5,6] the corresponding thiazole,[7] 2-(2'-hydroxyphenyl)benzimidazole,[8] and 2-(3'-hydroxy-2'-pyridyl)benzimidazole.[9] In all the members of this family of compounds, ESIPT is a very fast exothermic process.

In aprotic solvents, ground state HBO is an enol (the N—for "normal"—form) with an intramolecular hydrogen bond between the hydroxyl oxygen and the benzoxazole nitrogen; excitation gives rise to the excited enol form N*, which is successively transformed to the excited keto form T* (by ESIPT),[5] the ground state keto T (by fluorescent emission), and finally the starting N form (by ground state proton transfer); see Figure 1. The excitation spectrum of HBO in an argon matrix at 11 K shows bands at 31 250 and 29 850 cm⁻¹,[6] the later of which exhibits vibrational structure in the form of a short series of bands with a mean separation of 147 cm⁻¹ starting at 29 430 cm⁻¹. The emission spectrum shows bands with no vibrational structure at 21 460 and 20 240 cm⁻¹ (making the Stokes shift over 7000 cm⁻¹), together with an approximately 1000-fold weaker band between 30 000 and 25 000 cm⁻¹ (the region in which emission by the N form is expected). The rate constant of the ESIPT process under these conditions is estimated as at least 10^{11} s⁻¹. Only one study (an X-ray investigation[10]) has provided experimental structural information on HBO.

HBO has been studied theoretically by means of MNDO/H calculations of geometrical, spectral, and dynamical features;[6] by AM1;[11–13] and by STO-3G *ab initio* calculations of the ground state and T_1 state.[14] Since semiempirical methods have well-known limitations (especially as regards the calculation of excited states), in this work we carried out an *ab initio* study including partial exploration of the potential surfaces for the ground state (S_0) and the first excited singlet state (S_1), calculations of energies and geometries at stationary points, and an investigation of some aspects related to the dynamics of proton transfer processes. Reviewing the current results—supporting or revising them—through more rigorous static calculations is the main objective of this work.

Calculations

Calculations were carried out with GAUSSIAN92 programs.[15] Because of the size of HBO, its ground state was investigated mainly at the SCF/3-21G* level (with MP2/3-21G* calculations whenever possible and occasional supplementary 6-31G* and MP3/3-21G* calculations); the S_1 state, at the CIS/3-21G* level. It was unfortunately not possible to refine CIS S_1 energies with MP2 calculations, but even so "a satisfactory exploration of potential energy surfaces and accurate electronic properties of excited states are possible by use of CI-singles gradients".[16] Vibrational frequencies were calculated numerically for strategic reasons. All geometrical optimization was performed without constraints, with the exception of the excited TS*, in which C_s restriction has been imposed.

Results and Discussion

Characteristics of the Stationary Points. Table 1 lists the relative stabilities determined at each level for the four structures investigated. Frequency calculations confirmed that all the SCF and CIS structures correspond to stationary points.

As expected, the SCF results predict that the most stable ground state form is the enolic tautomer N, followed by the enolic rotamer R with a relative energy of 16.5 kJ·mol⁻¹. The latter figure is very close to the 4.4 kcal·mol⁻¹ predicted for R by MNDO/H calculations.[6] MNDO/H failed to locate the keto form T (and hence the transition state TS); the SCF/3-21G* calculations found a keto form T and a transition state of only

enol(N)

keto(T)

$$N^* \xrightarrow{\text{ESIPT}} T^*$$

$$\Big\uparrow \text{excitation} \qquad \text{emission} \Big\downarrow$$
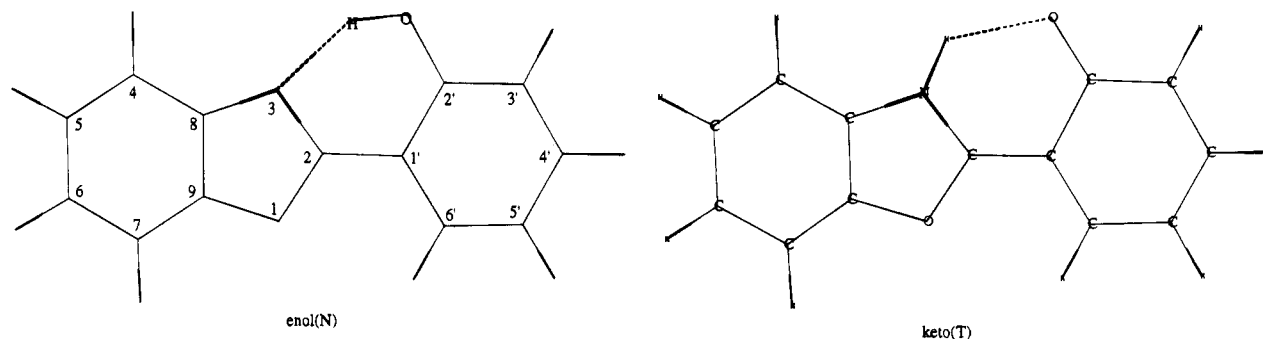
$$N \xleftarrow{\text{IPT}} T$$

Figure 1. (top) General structures of the enol (N) and keto (T) forms of 2-(2'-hydroxyphenyl)benzoxazole (HBO). (bottom) Chain of processes initiated by excitation of the enol form.

TABLE 1: Relative Energies (kJ·mol⁻¹)

form	sym	H-bond	HF/3-21G* S_0	HF/6-31G* S_0	MP2/3-21G* S_0	MP3/3-21G* S_0	CIS/3-21G* S_1
enol (N)	C_s	O−H··N	0.0	0.0	0.0	0.0	30.3
enol (R)	C_s	O−H··O	16.5				
keto (T)	C_s	O··H−N	46.8	65.0	89.8^a	78.4^a	0.0
TS (N−T)	C_s		57.5		82.7^a	80.1^a	45.9

^{a} Single-point calculations directly from SCF/3-21G* geometries. No stationary points were found by MP2.

TABLE 2: Some Features of the Hydrogen Bonds (HB) in the S_0 State^a

molecule	HB type	ΔE	r(OH)	Δr(OH)	r(N/O··O)	Δr(N/O··O)	r(N/O··H)	Δr(N/O··H)
N	O−H··N	58.66	0.980	+0.016	2.671	−0.23	1.843	−0.86
R	O−H··N	41.50	0.969	+0.005	2.608	−0.19	1.800	−0.80

^{a} ΔE = HB energies with respect to the corresponding open structures. ΔR's = differences with respect to the sum of van der Waals radii. Energies in kJ·mol⁻¹ and distances in angstroms.

slightly higher energy than T. The SCF/6-31G* confirm the same features.

MP2 calculations starting from the optimized SCF geometries for T led to the enol form; that is, no stationary point for T was found (and hence none for TS either). This was attributed to the MP2 method's well-known tendency to lower barriers. The MP2 energies for T and TS listed in Table 1, which appear to corroborate the absence of any barrier, were calculated as single points directly from the corresponding SCF geometries. MP3/3-21G* single-point calculations have been carried out further on T and TS, under the same conditions as for MP2. Now the results show a very small and not very significant barrier, which could grow nevertheless through the optimization processes. A keto T form could therefore exist, but the T → N process should be a nearly barrierless one.

All the above structures exhibit C_s symmetry, which is also exhibited by T*, the structure identified by unconstrained CIS/3-21G* optimization and frequency calculation as the most stable minimum in the first excited singlet state; whereas MNDO/H calculations[6] found a C_1 minimum for T* with a nonplanar amino moiety and a planar transition structure for transition at nitrogen. The C_s structure found can be understood by considering that the C_s S_1 keto T* form meets all the requirements for the formation of a conjugate pseudoaromatic heterocyclic ring, as proposed by Shigorin[17] and Durmis et al.[18]

TABLE 3: SCF/3-21G* Dipole Moments and Net Atomic Charges

	enol (N) S_0	enol (N) S_1	TS S_0	TS S_1	keto (T) S_0	keto (T) S_1
μ/D	2.63	2.05	4.36	2.99	4.83	5.41
q_H	+0.455	+0.469	+0.513	+0.515	+0.460	+0.455
q_O	−0.790	−0.797	−0.801	−0.815	−0.742	−0.746
q_{N3}	−0.834	−0.873	−1.080	−1.024	−1.100	−1.092
q_{O1}	−0.730	−0.720	−0.728	−0.720	−0.733	−0.726

In this form the N atom could be qualitatively seen as holding out a sp^2-like structure with a π lone electron pair which enhances the conjugation through the whole system.

Table 2 lists geometrical parameters and energies for the O−H··N and O−H··O hydrogen bonds of N and R in the ground state. All the distances between nonbonded atoms are less than the corresponding sums of van der Waals radii, and both these differences and the differences between the hydrogen-bonded and open form O−H distances show that the O−H··N bond is stronger than the O−H··O bond, according to the lower electronegativity of the N atom. The greater stability of the N form, which is corroborated by the estimated energy differences with respect to the open forms, appears to derive wholly from the hydrogen bond, since the calculated energies of the two open forms were practically identical.
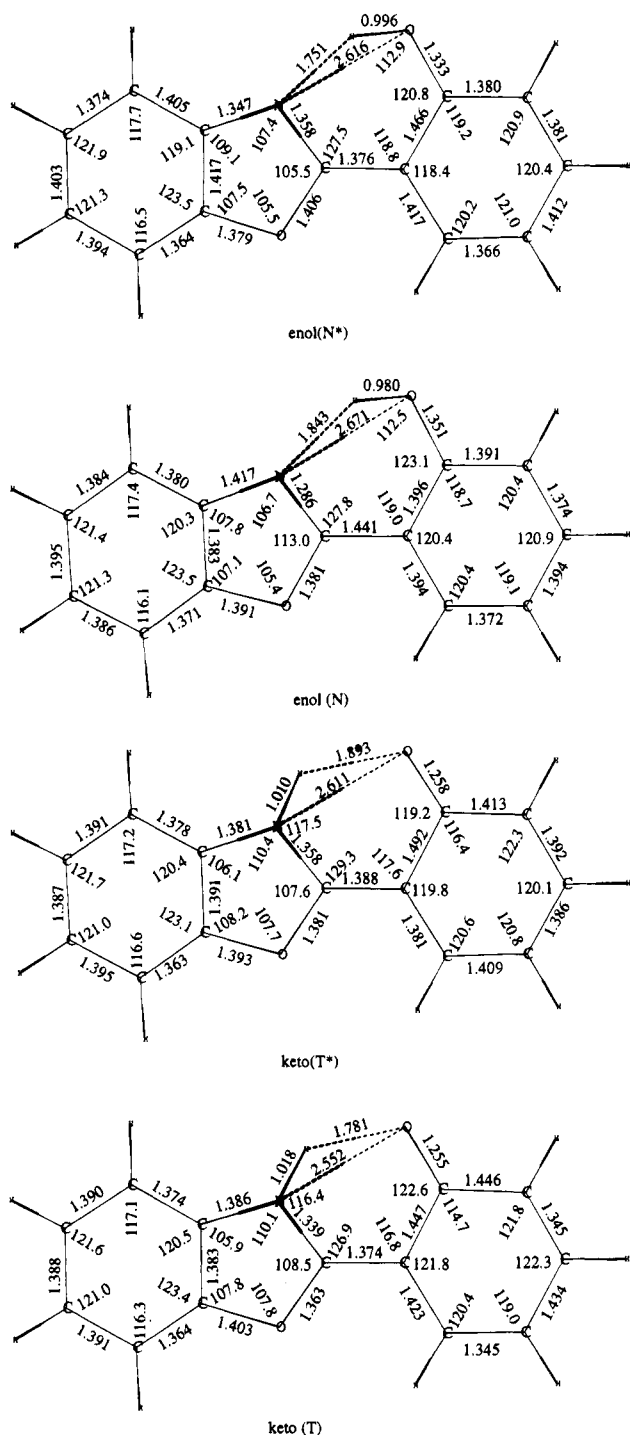
enol(N*)

enol (N)

keto(T*)

keto (T)

Figure 2. Geometrical parameters. Distances are in angstroms; angles, in degrees. (a, top) Enol in the S_0 (N) and S_1 (N*) states. (b, bottom) Keto in the S_0 (T) and S_1 (T*) states.

Table 3 lists parameters related to charge distribution. In spite of the limitations of the calculations performed, it seems clear that the environments of the heteroatoms are strongly polarized and that both the ground state and excited state keto forms have a large dipole moment.

Figure 2a,b shows the optimized SCF/3-21G* and CIS/3-21G* geometries for the ground state and singlet excited state enol (a) and keto (b) forms of HBO. The SCF/6-31G* and MP2/3-21G* results differ from these in the expected ways: the SCF/6-31G* geometries show shorter bonds to heteroatoms and the MP2/3-21G* data show significantly longer bonds of all kinds;[20] 3-21G* inaccuracies due to the crudity of the basis and to the lack of correlation partially cancel each other out.[21-25]

TABLE 4: Some In-Plane a' Vibrations[a]

struc-ture	state	ν/cm^{-1}	normal coordinates(main contributions)
N	S_0	125	$Q_{47} \simeq 0.85(321') - 0.34(197) - 0.21(21'2') - 0.17(2'OH) - 0.13(1'2'O)$
N	S_1	123	$Q_{47} \simeq 0.80(321') - 0.24(21'2') - 0.21(OH) - 0.19(19) - 0.18(197)$
N	S_0	298	$Q_{46} \simeq 0.54(2'1'6') - 0.40(21') - 0.29(1'6'5') - 0.28(1'2'3') - 0.22(197)$
N	S_1	308	$Q_{46} \simeq 0.57(2'1'6') - 0.39(21') - 0.38(1'2'3') - 0.23(1'6'5') + 0.19(6'5'H)$
N	S_0	3601	$Q_1 \simeq 0.99(OH)$
N	S_1	3270	$Q_1 \simeq 0.99(OH)$
T	S_0	121	$Q_{47} \simeq 0.80(321') + 0.34(2NH) - 0.22(21'2') - 0.19(197) - 0.17(1'2'3')$
T	S_1	124	$Q_{47} \simeq 0.81(321') - 0.20(197) - 0.19(1'2'O) - 0.19(19) - 0.18(1'2')$
T	S_0	301	$Q_{46} \simeq 0.59(2'1'6') + 0.29(123) - 0.27(1'2'3') - 0.27(1'6'5') - 0.20(21')$
T	S_1	305	$Q_{46} \simeq 0.54(2'1'6') - 0.32(1'6'5') - 0.31(21') + 0.28(123) - 0.23(1'2'3')$
T	S_0	3660	$Q_1 \simeq 0.99(NH)$
T	S_1	3610	$Q_1 \simeq 0.99(NH)$
TS	S_0	−1289	$Q \simeq 0.95(OH) - 0.25(2'OH)$
TS	S_1	−1436	$Q \simeq 0.92(OH) - 0.36(2'OH)$

[a] Frequencies unscaled. Coordinates in angstroms and radians.

In spite of these differences, the results of the more powerful calculations agree in general with the SCF/3-21G* findings, as do those of calculations carried out at the STO-3G level (with C_s symmetry imposed)[14] and by semiempirical methods[6,12] (the later are indeed very close to the geometries reported here). By contrast, the geometries observed by X-ray techniques[10] differ considerably from all the theoretical findings; in particular, the observed geometry of the 2'-hydroxyphenyl ring appears not to be compatible with either N, T, or a mixture of the two.

Geometrically, excitation from N to N* mainly affects the region of the ring closed by the hydrogen bond, especially as regards bond lengths and the angles 123 and 1'2'O. In particular, the O···N and H···N distances are both shortened, which facilitates proton transfer.

The alteration of electronic distribution by excitation (Table 3) is also reflected in modified vibrational behavior. By way of illustration, Table 4 lists the basic characteristics of some a' modes of N and T in the S_0 and S_1 states, including the modes of lowest frequency and those corresponding to OH or NH stretching. Note that excitation of the enol form facilitates OH stretching but not in-plane distortion in the region of the ring closed by the hydrogen bond. The above frequencies maintain qualitative agreement with the main experimental trends known for HBO. Nevertheless, it is well-known that *ab initio* (and semiempirically) calculated values are too high, as they correspond to harmonic frequencies; these values cannot be directly compared to the experimental anharmonic ones. As a rough approximation, they are frequently scaled by a factor lower than 1, depending on the level of calculation. The factor commonly accepted for HF calculations is 0.89, which for the OH stretching of the enol N leads to a wavenumber of 3204 cm^{-1}, lying within the experimental limits of 3266−3015 cm^{-1}.[18] The scaled value for the NH stretching vibration of the keto form is 3257 cm^{-1}, which is also within the range 3484−3242 cm^{-1} reported for very similar systems.[18] As the S_1 excited states are concerned, to the best of our knowledge, a specific scaling factor for CIS calculations has not been published so far. Furthermore, experimental data on vibrational frequencies are lacking; the value of 2650 cm^{-1} given in ref 6 for the OH stretching in the S_1 state corresponds in fact to this vibration in the similar system 2,5-bis(2-benzoxazolyl)hydroquinone, and it has been estimated
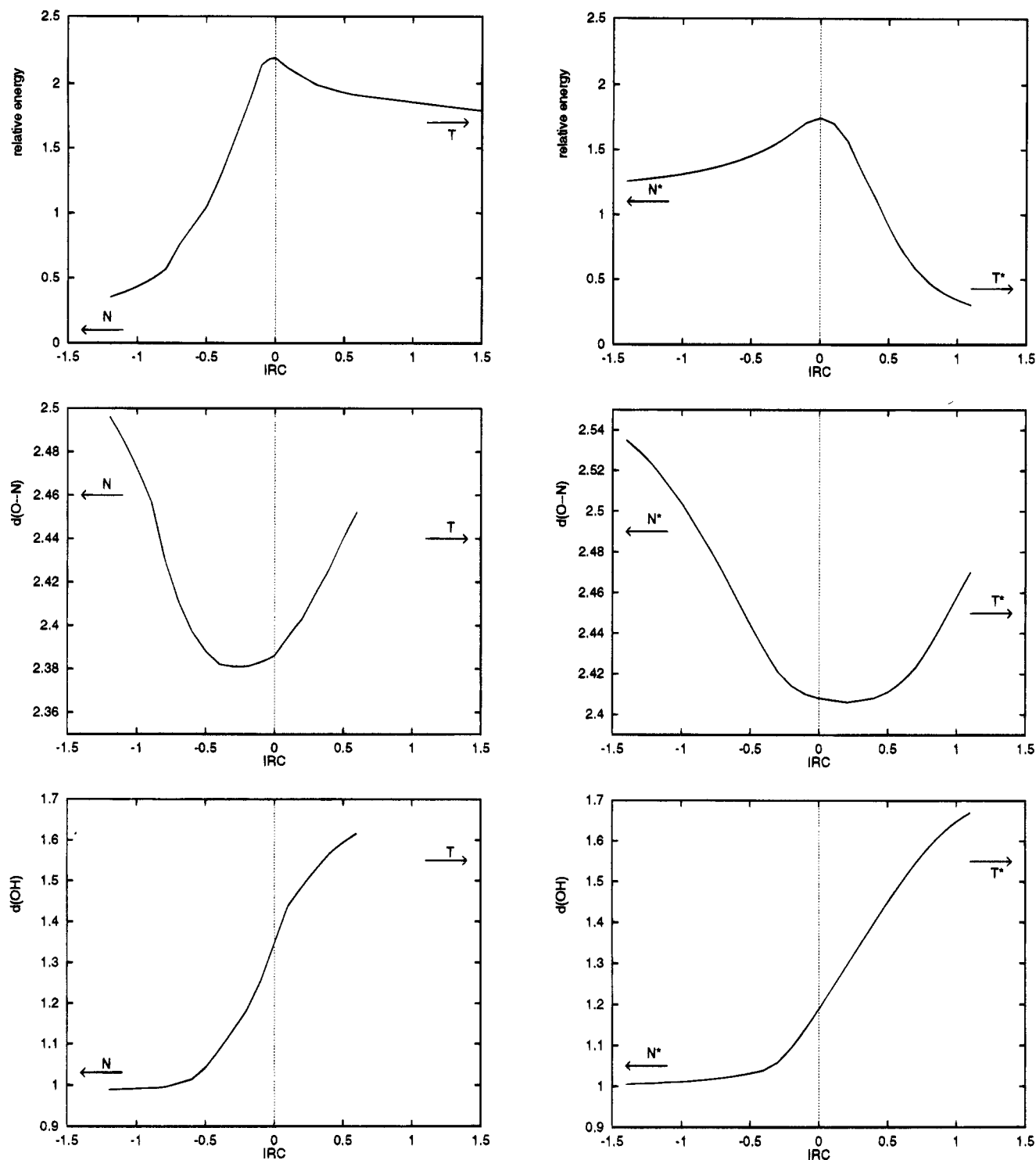
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Figure 3. Evolution of the relative energy and the O···N and O···H distances along the IRC. Energy in hartrees, distances in angstroms, and IRC in $(amu)^{1/2}$ Å. (a, left) Ground state. (b, right) S_1 excited state.

by Ernsting[19] from the blue shift of the 0—0 band on deuteration, assuming that the complete deuteration shift comes exclusively from the differences in the zero-point energies of the OH stretching mode in the ground and excited states. Therefore, the above mentioned value has to be considered only as an estimated lower limit for the OH stretching frequency of HBO in the S_1 excited state.

Proton Transfer. Figure 3a,b shows plots of energy and the O···N and O···H distances against the reaction coordinate for proton transfer in the ground state (a) and the first excited singlet state (b). Even taking into account the limited accuracy of the methods used, it is clear that the barriers to both the N* → T* and T → N process are very low, greater than the energies

of the lowest frequency vibrations but similar to, or smaller than, those of the stretching modes of the HBO skeleton. In view of this, and of the marked asymmetry of the potential function along this reaction coordinate, it may be hypothesized that, in keeping with available experimental data,[6] proton transfer comes about through vibrational relaxation rather than thermal activation. It must be emphasized that the O···N distances are shorter in N* and T than in N and T* (Figure 2a,b), and this seems to be responsible for lowering the barriers, which in addition should fluctuate as the O···N distances vibrate according to a' low-frequency modes (Figure 4). Furthermore, the frequencies of some of the N* modes that might be involved in the transfer process are lower than in N (Table 4).
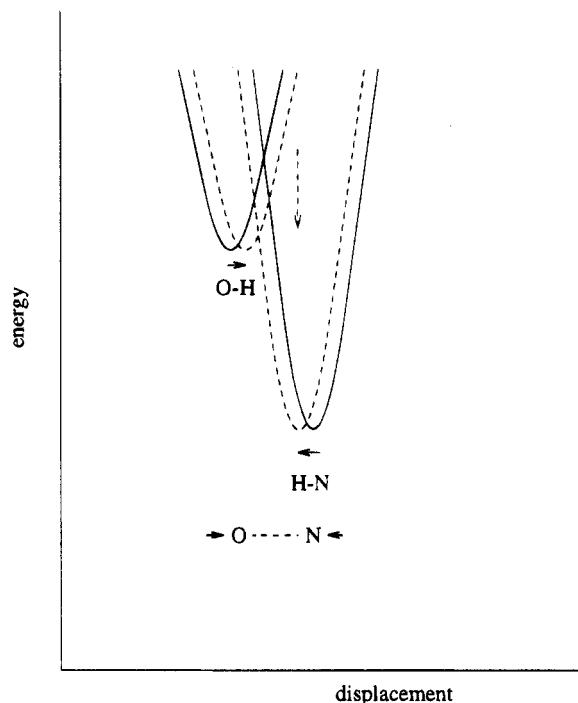
Figure 4. Outline of the fluctuation of the barrier with O⋯N low-frequency vibration (N* → T* process). The barrier decreases as the O⋯N distance becomes shorter.

Analysis of the molecular geometry as a function of the reaction coordinate shows that the proton transfer processes take place in the plane of the molecule. The first phase of either process is the mutual approach of the O and N atoms, doubtless thanks to the low-frequency a′ vibrations; the O−H distance (in the N* → T* process) or the N−H distance (for T → N) remains practically constant during this phase. When the H atom has been brought within the chemical interaction range of the other electronegative atom, the chemical process proper occurs with the concourse of the stretching and bending vibrations involving O−H (or N−H for T → N); Table 4 shows the major contributions to the negative frequency modes of the transition state. Proton transfer is completed by the separation of the heavy atoms.

Finally, we note that although in this case the excited state proton transfer behavior appears to be explained adequately through the S$_1$ state of $\pi\pi^*$ character, the involvement of other excited states cannot be ruled out, as Sobolewski and Domcke have shown for a simpler molecular model.[26]

Conclusions

The *ab initio* reported calculations are useful in further supporting most of the current views on the ESIPT mechanism. They show that in the gas phase the enol form N of HBO is not only more stable than the keto form T but also more stable than the enolic rotamer form R, due to the O−H⋯N bond being more stable than O−H⋯O. In the S$_1$ state N*, proton transfer is favored by a sharp reduction in the barrier to the N* → T*

process, by the O⋯N distance being shorter than in N, and by the frequencies of the vibrations most probably involved in proton transfer being lower than in N. *Ab initio* results suggest an in-plane mechanism for the proton transfer process, for which three phases may be hypothesized: mutual approach of the N and O atoms due to in-plane bending modes; proton transfer *sensu stricto* in the transition state region, largely at the expense of O−H stretching; and the final separation of the N and O atoms.

References and Notes

(1) Caldin, E. F., Gold, V., Eds. *Proton-Transfer Reactions*; Chapman and Hall: London, 1973.

(2) Skulachev, V. P., Hinkle, P. C., Eds. *Chemiosmotic Proton Circuits in Biological Membranes*; Addison-Wesley: Reading, MA, 1981.

(3) Schneider, D. L. *Biochim. Biophys. Acta* **1987**, *895*, 1.

(4) Barbara, P. F.; Wals, P. K.; Brus, L. E. *J. Phys. Chem.* **1989**, *93*, 29.

(5) Williams, D. L.; Heller, A. *J. Phys. Chem.* **1970**, *74*, 4473.

(6) Arthen-Engeland, Th.; Bultman, T.; Ernsting, N. P.; Rodriguez, M. A.; Thiel, W. *Chem. Phys.* **1992**, *163*, 43.

(7) Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1980**, *102*, 5631.

(8) Das, K.; Sarkar, N.; Majumdar, D.; Bhattacharyya, K. *Chem. Phys. Lett.* **1992**, *198*, 443.

(9) Rodriguez, F.; Rios, M. C.; Mosquera, M.; Rios, M. A. *J. Phys. Chem.* **1994**, *98*, 8666.

(10) Mordzinski, A. Excited State Intramolecular Proton Transfer: The Structural and Dynamic Aspects, Doctoral Thesis, Polska Akademia Nauk, Instytut Chemii Fizycznej, Warszawa, 1990.

(11) Lavtchieva, L.; Enchev, V.; Smedarchina, Z. *J. Phys. Chem.* **1993**, *97*, 306.

(12) Enchev, V. *Indian J. Chem.* **1994**, *33B*, 336.

(13) Das, K.; Sarkar, N.; Ghosh, A. K.; Majumdar, D.; Nath, D. N.; Bhattacharyya, K. *J. Phys. Chem.* **1994**, *98*, 9126.

(14) Nagaoka, S.; Itoh, A.; Mukai, K.; Nagashima, U. *J. Phys. Chem.* **1993**, *97*, 11385.

(15) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN-92*, Revision B; Gaussian, Inc.: Pittsburgh, PA, 1992.

(16) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(17) Shigorin, D. N. *Spectrochim. Acta* **1959**, *14*, 198.

(18) Durmis, J.; Karvas, M.; Manasek, Z. *Collect. Czech. Chem. Commun.* **1973**, *38*, 243.

(19) Ernsting, N. P. *J. Phys. Chem.* **1985**, *89*, 4932.

(20) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

(21) Bicerano, J.; Schaefer, H. F., III; Miller, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2250.

(22) Frisch, M. J.; Scheiner, A. C.; Schaefer, H. F., III; Binkley, J. S. *J. Chem. Phys.* **1985**, *82*, 4194.

(23) Rios, M. A.; Rodriguez, J. *J. Mol. Struct. (THEOCHEM)* **1991**, *228*, 149.

(24) Graña, A. M.; Rios, M. A. *Struct. Chem.* **1991**, *2*, 575. Estevez, C. M.; Rios, M. A.; Rodriguez, J. *Ibid.* **1992**, *3*, 381.

(25) Rios, M. A.; Rodriguez, J. *Can. J. Chem.* **1991**, *69*, 201. *Ibid.* **1993**, *71*, 303.

(26) Sobolewski, A. J.; Domcke, W. *Chem. Phys. Lett.* **1993**, *211*, 82.

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