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AM1 study of ground state intramolecular proton transfer reaction in 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(2'-hydroxyphenyl)benzotriazole

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Abstract

The activation parameters for ground state intramolecular proton transfer reactions of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (TIN) and 2-(2'-hydroxyphenyl)benzotriazole (HPB) are calculated by means of the AM1 method. It is shown that the rate constants of these reactions calculated by the Eyring equation suffer a small variation when the entropy term is taken into account. The AM1 calculated structural parameters for the enol tautomer of TIN are compared with the available X-ray experimental data.

Introduction

2-(2'-Hydroxy-5'-methylphenyl) benzotriazole (trade name TINUVIN P or TIN) is a widely used ultraviolet stabilizer of polymers. This compound has been investigated in solution and in solid matrices by a variety of spectroscopic techniques [1–14].

In the ground state TIN exist in the enol form **E**. After the absorption of UV light, the next rapid step in this molecule is an excited state intramolecular proton transfer (IPT) in the S_1 state, producing the energetically favorable keto form **K**. The strongly Stokes-shifted emission in the red spectral region has been attributed to the keto tautomer. The reaction cycle of TIN is completed by ultrafast (between 500 fs and 1.2 ps [14]) **K** → **E** back-proton transfer, proceeding via the electronic ground state. This extremely fast proton transfer in the ground state suggests a low potential barrier.

The mechanism of the proton transfer reactions

between the keto and enol tautomers in the ground state of TIN and 2-(2'-hydroxyphenyl)benzotriazole (HPB) was studied using the AM1 method [15], which can reproduce hydrogen bonding. This method has been successfully used in the interpretation of IPT reaction mechanisms [16–19]. Several studies have been reported indicating that the AM1 and high level ab initio results for geometries of minima and transition states are in good agreement [20–23].

Computational method

All calculations in this work were performed with the MOPAC 6.0 program package [24]. The geometries of the stable species were completely optimized using the keyword PRECISE. Stationary points on the AM1 energy surfaces were located by the EF (minima) and transition states routines [25] and were characterized by vibrational analysis to

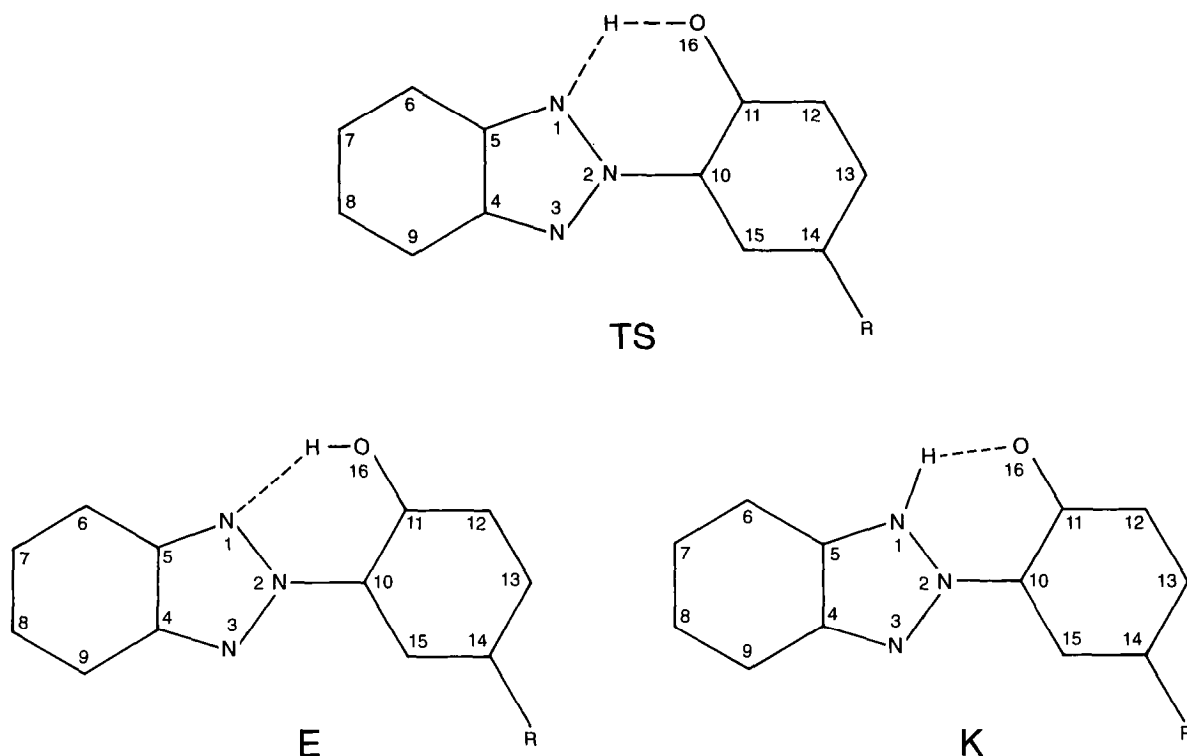


Fig. 1. Structure and numbering of the atoms of the enol **E** and keto **K** tautomers, and the transition state **TS** for 2-(2'-hydroxyphenyl)benzotriazole (HPB) ($R = H$) and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (TIN) ($R = CH_3$).

ensure the presence of a single negative eigenvalue of the force constant matrices of the transition states.

Results and discussion

It is found that the enol form **E** of TIN is more stable by $26.19 \text{ kcal mol}^{-1}$ than the keto form **K** (Fig. 1). The heat of formation of **E** is calculated to be $108.00 \text{ kcal mol}^{-1}$. The optimized geometrical parameters of these two tautomers and the transition state **TS** are summarized in Table 1. The corresponding data from the X-ray analysis of the enol form [5] are also shown. According to the crystal structure determination, TIN is planar. The comparison reveals very good agreement between the calculated and experimentally determined bond lengths of tautomer **E**. However, it can be seen from Table 1 that **E** and **K** are non-planar. It is calculated that the benzotriazole

moiety in **E** is twisted by 46.4° relative to the *p*-cresol ring. This contradiction with experiment is due to the fact that the AM1 method has been optimized to reproduce geometries of isolated molecules. In the solid state TIN is planar but Weichmann et al. [14] have detected an enol conformer of TIN with nonplanar geometry, emitting in the blue spectral range in solution. Other similar examples might be given. The biphenyl molecule also has a planar structure in the crystal state [26], whereas the dihedral angle is 44.4° in the vapor phase [27]. Recently, Csizmadia and co-workers [28] have reported that the AM1 calculated torsional angle about the central bond in biphenyl is 40.6° , in excellent agreement with the gas phase value. Dick [29] has also shown that in 3-hydroxyflavone the AM1-calculated dihedral angle of 29.2° between the phenyl ring and the hydroxyhormone moiety is reasonable for this molecule in solution AM1 probably predicts

Table 1
AM1-calculated structural parameters of the enol **E** and keto **K** tautomeric forms and TS of TIN

Parameter ^a	Exp ^b	E	K	TS
<i>Selected bond</i>				
N1–N2	1.344	1.348	1.399	1.361
N1–C5	1.359	1.371	1.418	1.382
N2–N3	1.331	1.346	1.318	1.317
N3–C4	1.360	1.372	1.413	1.398
C4–C5	1.416	1.478	1.450	1.463
C4–C9	1.414	1.422	1.399	1.410
C5–C6	1.412	1.422	1.394	1.409
C6–C7	1.375	1.368	1.392	1.378
C7–C8	1.427	1.429	1.405	1.418
C8–C9	1.372	1.368	1.390	1.378
C2–C10	1.426	1.446	1.401	1.443
C10–C11	1.404	1.413	1.466	1.441
C10–C15	1.397	1.410	1.437	1.415
C11–C12	1.398	1.411	1.458	1.432
C12–C13	1.385	1.384	1.352	1.369
C13–C14	1.402	1.403	1.435	1.418
C14–C15	1.391	1.393	1.365	1.381
C11–O16	1.359	1.369	1.255	1.300
N1–H	1.85	2.438	1.017	1.174
O16–H		0.966	2.011	1.444
C14–CH3	1.506	1.481	1.480	1.480
<i>Selected bond angle</i>				
N1–N2–N3		116.4	113.3	114.5
N2–N3–C4		104.6	106.8	105.7
N2–N1–C5		104.6	105.6	106.8
N1–C5–C6		133.1	132.7	133.8
N3–C4–C9		133.0	132.1	132.6
C4–C9–C8		118.0	117.6	117.8
C7–C8–C9		122.2	122.0	122.1
N3–N2–C10		121.6	124.7	126.7
N2–C10–C11		121.7	120.7	118.2
N2–C10–C15		118.8	119.3	120.5
C10–C11–C12		119.3	115.5	116.5
C11–C12–C13		120.3	122.4	121.2
C12–C13–C14		120.7	121.2	121.5
C10–C11–O16		126.5	123.6	122.9
C13–C14–CH3		120.0	118.3	119.2
C11–O16–H		110.7	115.6	112.1
<i>Selected dihedral angle</i>				
C11–C10–N2–N1	0.9	46.4	18.6	0.0
C10–N2–N3–N1		175.9	175.1	179.9
C4–N3–N2–N1		0.6	5.4	0.0
C5–N1–N2–N3		–0.8	–8.4	0.0
H–N1–N2–N3			–146.6	179.9
H–O16–C11–C10		–3.9		

^a The numbering of the atoms is given in Fig. 1. Bond lengths are in ångströms and angles are in degrees. ^b Ref. 5.

reliable values for the torsional angles in the gas phase or in solution. It is found that tautomer **K** has partly quinoid character (see Table 1), the benzotriazole moiety and the quinoid fragment being twisted by 18.6° relative to each other.

Calculations had also been performed for HPB. The structural modification has little effect. The dihedral angle between the benzotriazole fragment and the hydroxyphenyl ring is calculated to be 46.0° in **E** and 18.7° in **K** for HPB. Planar forms of tautomers **E** and **K** are also found for HPB. These planar forms are more unstable by 1.1 and 0.9 kcal mol^{–1} respectively than the nonplanar forms for tautomers **E** and **K**. A planar geometry for HPB has also been obtained by Bocian et al. [3] by the CNDO method, and this geometry was then used for the calculated S₀ and S₁ properties of HPB in the INDO/CI approximation.

It has been found that the transition state of the **K** → **E** reaction for TIN has a planar structure (see Table 1). Proton translocation occurs along the H-bond. The calculated imaginary frequency is 1726.97 i cm^{–1}. The N···H and O···H distances in **TS** are 1.174 and 1.444 Å respectively. The barrier height for the proton transfer from **K** to **E** is calculated to be 8.49 kcal mol^{–1}. The Gibbs free energy at 298 K has also been calculated by using standard statistic mechanical formulae as implemented in MOPAC. The entropy term ΔS[‡] in the equation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

has a small value (see Table 2) and does not influence the value of the energy barrier. At 298 K, ΔG[‡] for the reaction **K** → **E** is calculated to be 8.67 kcal mol^{–1}. The classical rate constant at 298 K ($k = 2.24 \times 10^6 \text{ s}^{-1}$) is calculated by the Eyring equation $k = (k_B T/h) \exp(-\Delta G^{\ddagger}/RT)$ where k_B and h are the Boltzmann and Planck constants respectively. The values for k shown in Table 2 suffer a small variation when taking into account the $T\Delta S^{\ddagger}$ term. Similar results are also obtained for intramolecular proton transfer from tautomers **K** to **E** of HPB. Recently, it has been shown by us [19] that for the process **K** → **E** for salicylideneaniline (SA) the $T\Delta S^{\ddagger}$ term also has a

Table 2
Activation parameters for $K \rightarrow E$ at 298 K

Molecule	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	k (s ⁻¹)		ν^\ddagger (cm ⁻¹)
				$\Delta S^\ddagger = 0$	$\Delta S^\ddagger \neq 0$	
TIN	8.49	-1.01	8.67	3.72×10^6	2.24×10^6	1726.97i
HPB	8.27	-1.34	8.79	5.38×10^6	2.73×10^6	1716.18i
SA	19.50 (20.05) ^a	-0.57	19.67	3.15×10^{-2}	2.37×10^{-2}	2061.98i

^a Experimental value [30].

small value. For comparison, this result is also given in Table 2. It has been shown that in this last case the AM1-calculated ΔH^\ddagger is in very good agreement with the experimentally obtained value (see Table 2).

References

- 1 T. Werner, J. Phys. Chem., 83 (1979) 320.
- 2 A.L. Huston, G.W. Scott and A. Gupta, J. Chem. Phys., 76 (1982) 4978.
- 3 D.F. Bocian, A.L. Huston and G.W. Scott, J. Chem. Phys., 79 (1983) 5802.
- 4 S.R. Flom and P.F. Barbara, Chem. Phys. Lett., 94 (1983) 488.
- 5 G. Woessner, G. Goeller, P. Kollat, J.J. Stezowski, M. Hauser, U.K.A. Klein and H.E.A. Kramer, J. Phys. Chem., 88 (1984) 5544.
- 6 G. Woessner, G. Goeller, J. Rieker, H. Hoier, J.J. Stezowski, E. Daltrozzi, M. Neureiter and H.E.A. Kramer, J. Phys. Chem., 89 (1985) 3629.
- 7 D.B. O'Connor, G.W. Scott, D.R. Coulter, A. Gupta, S.P. Webb, S.W. Yeh and J.H. Clark, Chem. Phys. Lett., 121 (1985) 417.
- 8 K.P. Ghiggino, A.D. Scully and I.H. Leaver, J. Phys. Chem., 90 (1986) 5089.
- 9 M. Lee, J.T. Yardley and R.M. Hochstrasser, J. Phys. Chem., 91 (1987) 4621.
- 10 A.L. Huston and G. W. Scott, J. Phys. Chem., 91 (1987) 1408.
- 11 G. Goeller, J. Rieker, A. Maier, J.J. Stezowski, E. Daltrozzi, M. Neureiter, H. Port, M. Weichmann and H.E.A. Kramer, J. Phys. Chem., 92 (1988) 1452.
- 12 Y.R. Kim, J.T. Yardley and R.M. Hochstrasser, Chem. Phys., 136 (1989) 311.
- 13 M. Weichmann, H. Port, E. Laerner, W. Frey and T. Elsaesser, Chem. Phys. Lett., 165 (1990) 28.
- 14 M. Weichmann, H. Port, W. Frey, E. Lärmer and T. Elsässer, J. Phys. Chem., 95 (1991) 1918.
- 15 M.J.S. Dewar, E. Zoebisch, E. Healy and J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902.
- 16 J. Elguero, P. Goya, A. Martinez and I. Rozas, Chem. Ber., 122 (1989) 919.
- 17 R.L. Redington and C.W. Bock, J. Phys. Chem., 95 (1991) 10284.
- 18 M.S. Topaler, V.M. Mamaev, Ye.B. Gluz, V.I. Minkin and B.Ya. Simkin, J. Mol. Struct. (Theochem), 236 (1991) 393.
- 19 V. Enchev, C.R. Acad. Bulg. Sci., 46 (1993) 67.
- 20 D.C. Spellmeyer and K.N. Houk, J. Am. Chem. Soc., 110 (1988) 3412.
- 21 M.J.S. Dewar and E.F. Healy, Chem. Phys. Lett., 141 (1987) 521.
- 22 M.J.S. Dewar and B.M. O'Connor, Chem. Phys. Lett., 138 (1987) 141.
- 23 C.H. Reynolds, J. Am. Chem. Soc., 112 (1990) 7903.
- 24 J.J.P. Stewart, MOPAC 6.0, QCPE No. 455, Bloomington, IN, 1990.
- 25 J. Baker, J. Comput. Chem., 7 (1986) 385.
- 26 J. Trotter, Acta Crystallogr., 14 (1961) 1135.
- 27 A. Almendinger, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.L. Cyvin and S. Samdal, J. Mol. Struct., 128 (1985) 59.
- 28 T.-H. Tang, M. Nowakowska, J.E. Guillet and I.G. Csizmadia, J. Mol. Struct. (Theochem), 232 (1991) 133.
- 29 B. Dick, J. Phys. Chem., 94 (1990) 5752.
- 30 M.D. Cohen, G.M.J. Schmidt and S. Flavini, J. Chem. Soc., (1964) 2041.