[1]H nmr Studies of Some Heterocyclic Compound Part-IV.
Tautomerism in 5,6-Dimethyl-1,2,3-Benzotriazole.

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Summary: The exchange of the NH in 5,6 - dimethyl - 1,2,3 - benzotriazole has been studied by total line shape analysis of ^{1}H nmr spectra. It has been observed that the rate of this process is dependent on concentration, temperature, and the water present in solvent as impurity. The activation parameters (E_a, $\triangle*H$, $\triangle*S$, $\triangle*G_{298}$) for the title compound have been obtained.

Introduction

There is a rapid tautomerism in 1,2,3, benzotriazole[1,2] where the NH proton exchanges its position between nitrogen atoms 1 and 3.

It has been observed that there are several factors such as concentration, temperature and acidic or basic impurities which influence the rate of tautomerism in this system. In this paper we present the effect of substituent on the NH proton exchange, in the system in question.

Experimental

Preparation of Compound:

A mixture of 1,2 dimethyl - 4,5-diamino-o-xylene (11.5 gm), glacial acetic acid (9.8 ml) and water (25 ml) was shaken thoroughly and cooled to 50°C in ice cold water.

A solution of sodium nitrite (6.4 gm) in water (10 ml) was added slowly in order to avoid rapid rise of temperature. The mixture was left at room temperature for twenty four hours. The ppt was filtered and washed with distilled water until it was neutral, and then dried in vaccum at 50°C. The dry material was recrystallised from benzene but the crystals were not colourless. The recrystalisation from benzene was repeated until pure and colourless compound was obtained, then dried in vacuum at 60°–70°C (mpt 156°–157°C).

Recording ^{1}H NMR Spectra:

A 0.53M solution of 5,6 dimethyl benzotriazole

was prepared in THF according to the procedure described in our previous study[2]. Two other concentrations 0.485M and 0.432M were obtained by successive dilution of the first concentration. The dilution was carried out by syringing the required amount of the solvent into the nmr tube through the suba seal.

A varian XL-100 NMR spectrometer was used for this study. All the spectra reported here were recorded at 50H$_z$ sweep width.

The spectra of aromatic protons of 5,6 dimethyl benzotriazole were recorded at various temperature in the range of + 50°C to −50°C, for each concentration. A methanol capillary containing TMS as a reference was used for temperature measurement.

Line Shape Analysis of 5,6 Dimethyl Benzotriazole.
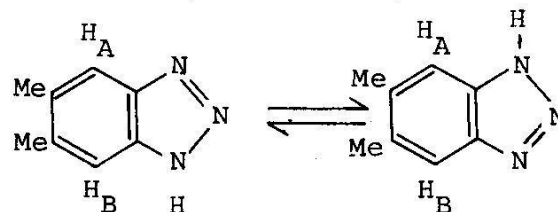
Scheme 1

The protons H$_A$ and H$_B$ appear as a singlet when the exchange of NH proton between 1 and 3-N atoms is fast. The two resonances separate into two broad singlets in the zero exchange limit. Since the coupling is very small in this system it was analysed with a computer program called, 'CHEM 28'[3] based on Gutowsky and Holm's equation[4] which is applicable to the uncoupled systems.

The following input parameters were used in this program.

i.   Complete experimental spectrum at each temperature in digitised form;

ii.   Separation in Hz between two proton resonances νA and νB in the zero exchange limit.

iii. Separation in Hz between νA and νB at each temperature;

iv.   The change in separation between two peaks, as a function of temperature;

v.   Widths νA½ and νB½ of the two peaks at their half heights in the zero exchange limit;

vi.   Total number of temperature at which the spectra have been recorded. The program cannot handle more than twenty one different spectra in one set of data;

vii. Total number of points to represent each spectrum;

viii. The base line of each spectrum;

ix.   The concentration of the solution.

The spectrum at each temperature was manually digitised. To make the digitisation easier, a smooth line was drawn through each noisy experimental spectrum. At least 40-50 points were taken to represent each spectrum. The base lines should be the same because an out of phase spectrum will introduce large errors between the calculated and experimental spectra. The separation (νAB) between the two peaks A and B was measured in H_Z at each temperature below coalescence. This was plotted against temperature as shown in fig.1. The curve in fig.1 shows that separation increases with decrease in temperature to a certain stage and then starts decreasing. This decrease in separation is due to the temperature effect and it is not influenced by the exchange process because the exchange is significantly slow in this region of spectrum. In order to obtain separations above coalescence temperature this curve was extrapolated. This curve was obtained at all three concentrations (0.4326, 0.53M, 0.485M). Table 1 shows the experimental and calculated peak separations in 5,6 dimethyl benzotriazole. The calculated peak separations were used in the computer program 'CHEM 28'. The calculated peak separation estimates the variation in the two peaks positions with temperature if there was no exchange occuring in the system. The change of separation of two peaks was determined from the slope of the extrapolated straight line.
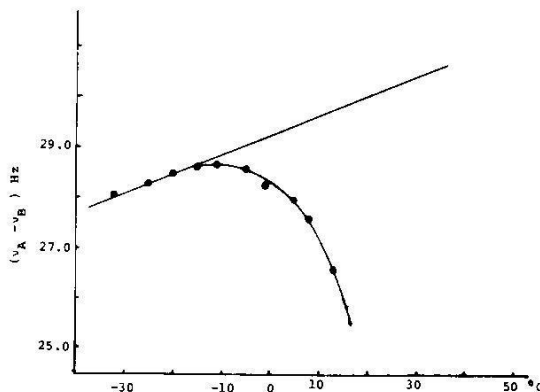

Fig.1: The variation of the chemical shift difference$(\nu_A - \nu_B)$ HZ of the protons H_A and H_B in 5,6 dimethyl benzotriazole (0.4326M) with temperature.

Table. 1

$C_1 = 0.5300M$ 5,6 dimethyl benzotriazole

No.	Temperature ($^\circ$C)	Separations between two peaks $(\nu_A - \nu_B)$ HZ	
		(From spectrum)	(From graph)
1.	−46.00	27.0	27.37
2.	−34.00	27.6	27.57
3.	−22.00	27.85	27.80
4.	−15.00	27.90	27.90
5.	−12.00	27.80	27.97
6.	−07.00	27.20	28.05
7.	−05.00	27.10	28.10
8.	−03.00	26.70	28.13
9.	+02.00		28.20
10.	08.00		28.32
11.	13.00		28.40
12.	15.00		28.45
13.	18.00		28.50
14.	20.00		28.52
15.	23.00		28.57
16.	27.00		28.65
17.	32.00		28.75
18.	34.00		28.77
19.	39.00		28.85
20.	44.00		28.95
21.	50.00		29.05

The program 'CHEM 28' calculates the average residence time (τ) of the exchanging proton at each temperature; the rate constant (K) of the exchange process at each temperature is obtained.

A sub-routine of 'CHEM 28', called TDPAR for thermodynamic parameters, calculates Arrhenius parameter-energy of activation (E_a.) frequency factor (A) and Eyring's activation parameter entropy of activation ($\triangle*S$), enthalpy of activation ($\triangle*H$) free energy of activation ($\triangle*G$), utilising the rate constant at different temperatures.

For a given set of data a calcomp plot is also obtained which consists of theoretical (upper) and experimental (lower) spectra at each temperature as shown in figs. 2,3,4 for three different concentrations. The root mean square (RMS) error listed with each spectrum indicates the deviation between fitted and experimental spectra; only the spectra with small RMS errors were retained and those with higher RMS ($>$ 8.0) values were rejected. At each concentration an Arrhenius plot (logk VS $\dfrac{1}{T}$) was drawn and only the points falling very close to the straight line were retained and others were rejected.

Thus only the spectra having low RMS error values and producing good Arrhenius plots (figs. 5,6,7) were used to obtain the final results reported in this paper.

The order of the exchange process was found to be approximately three. Tables 2,3,4 show the third order rate constants (K) at various temperature (T) for three different concentrations. The activation parameters are listed in table 5.

Substituent effect:

The activation parameters appear to be varying with concentration for 5,6 dimethyl benzotriazole. These parameters are very sensitive to systematic errors[5] and for a given compound one cannot say that whether or not these variations are real.

However the differences between E_a, $\triangle*S$ and $\triangle*H$ values of benzotriazole[2] and its 5,6 dimethyl derivative are so large that one cannot attribute them to systematic errors. Some information may be obtained from these variations. The energy of activation. (E_a = 26.358$\overset{+}{-}$ 1.082 KJ mol^{-1}) for 5,6 dimethyl is considerably higher than that (E_a = 16.867 = 3.617 KJ mol^{-1}) of 1,2,3 benzotriazole. This shows that the proton transfer in the former compound is slower than that in the latter one.
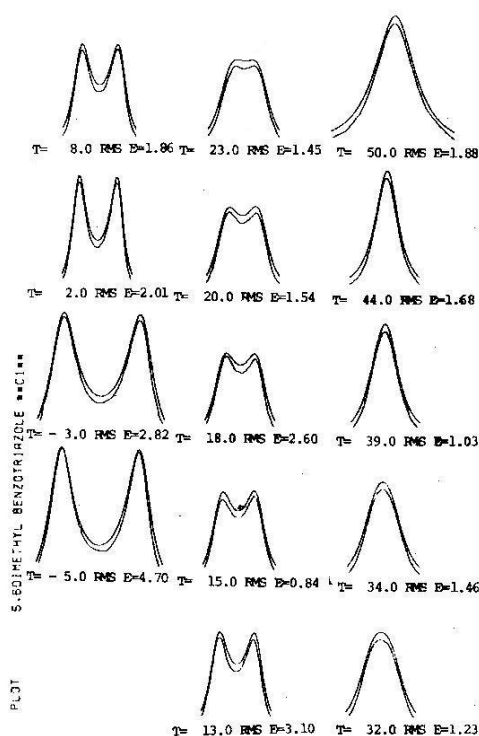

Fig.2: The calculated (upper) and experimental (lower) line shapes of 5,6 dimethyl benzotriazole (0.53M in THF) at various temperatures.
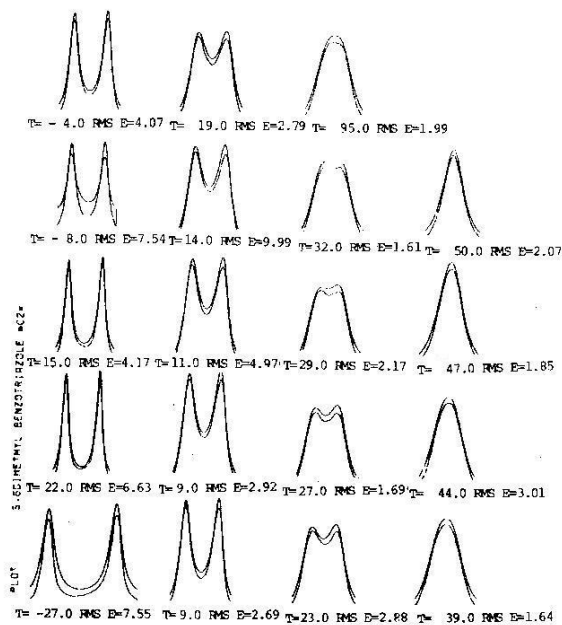

Fig.3: The calculated (upper) and experimental (lower) line shapes of 5,6 dimethyl benzotriazole (0.4850M in THF) at various temperatures.
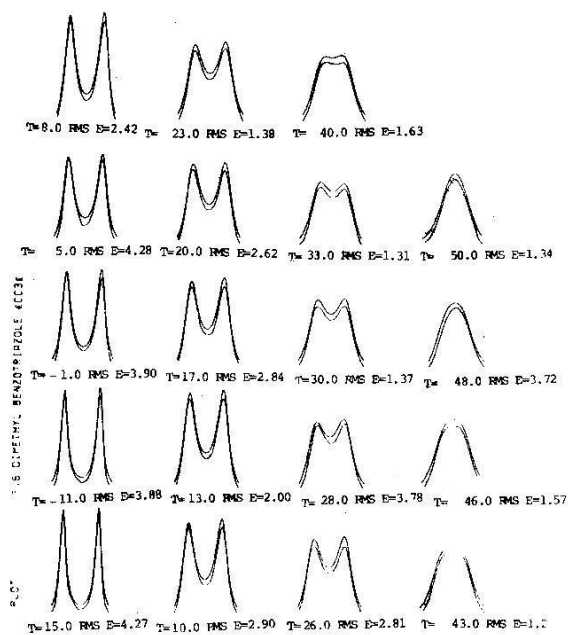
Fig.4: The calculated (upper) and experimental (lower) line shapes of 5,6 dimethyl benzotriazole (0.4326M in THF) at various temperatures.
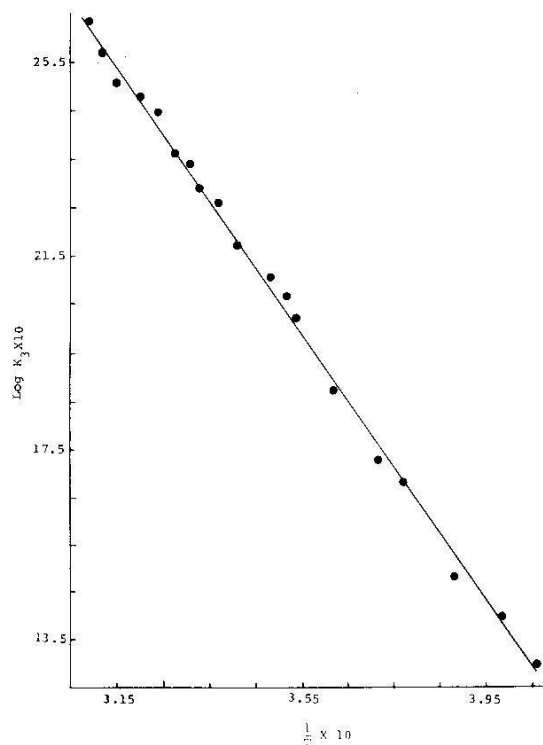
Fig.6: The Arrhenius plot (log K VS 1/T) obtained from the data in table 3 for 5,6 dimethyl benzotriazole (0.4850M in THF).
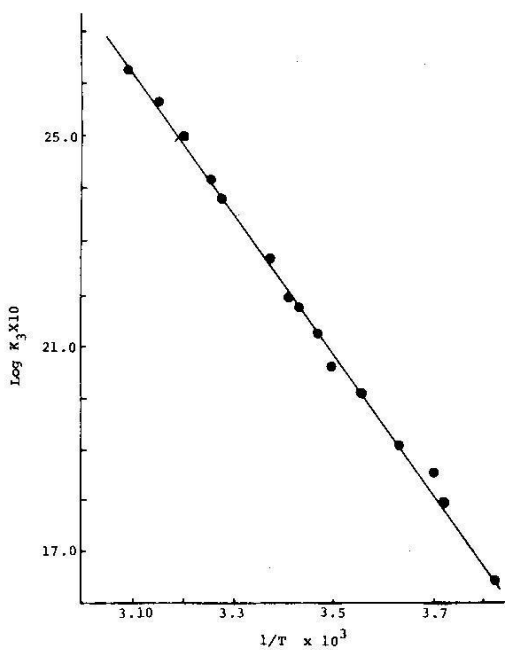
Fig.5: The Arrhenius plot (log K VS 1/T) obtained from the data in table 2 for 5,6 dimethyl benzotriazole (0.53M in THF).
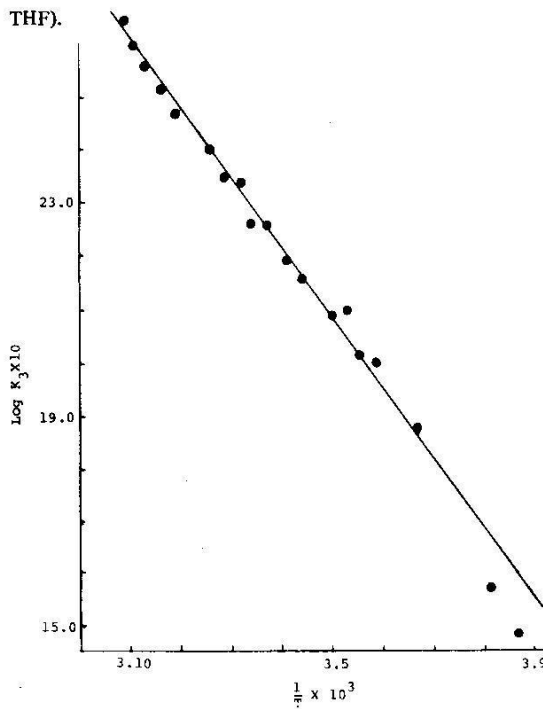
Fig.7: The Arrhenius plot (log K VS 1/T) obtained from the data in table 4 for 5,6 dimethyl benzotriazole (0.4326M in THF).

Table. 3

$C_2^{'}=0.4850M$ 5,6 dimethyl benzotriazole

T°C	T°K	1/T	τ Sec	$Kl^2 mol^{-2} sec^{-1}$	log K	log K/T
−27.00	246.16	0.0040624	0.1070	19.8635	1.2980	−1.0931
−22.00	251.16	0.0039815	0.0846	25.1229	1.4000	− .9998
−16.00	257.16	0.0038886	0.0700	30.3628	1.4823	− .9278
−08.0	265.16	0.0037713	0.0439	48.4145	1.6849	− .7385
−04.0	269.16	0.0037153	0.0387	54.9198	1.7397	− .6902
+03.0	276.16	0.0036211	0.0282	75.3687	1.8772	− .5639
9.0	282.16	0.0035441	0.0203	104.6994	2.0199	− .4305
11.0	284.16	0.0035191	0.0182	116.7801	2.0673	− .3861
14.0	287.16	0.0034824	0.0166	128.0360	2.1073	− .3507
19.0	292.16	0.0034228	0.0141	150.7348	2.1782	− .2874
23.0	296.16	0.0033766	0.0116	181.8133	2.2596	− .2119
27.00	300.16	0.0033316	0.0109	194.9906	2.2900	− .1873
29.00	302.16	0.0033095	0.0096	221.3956	2.3451	− .1350
32.00	305.16	0.003277	0.0092	231.0215	2.3636	− .1208
35.00	308.16	0.0032451	0.0076	279.6576	2.4466	− .0421
39.00	312.16	0.0032035	0.0070	303.6283	2.4823	− .0120
44.00	317.16	0.0031530	0.0066	322.0300	2.5078	+ .0066
47.00	320.16	0.0031234	0.0057	372.8769	2.5715	+ .0661
50.00	323.16	0.0030944	0.0048	442.7913	2.6462	+ .1367

Table. 2

$C_1 = 0.530M$ 5,6 dimethyl benzotriazole

T°C	T°K	1/T	τ Sec	$Kl^2 mol^{-2} sec^{-1}$	log K	log K/T
−12.0	261.16	0.0038291	0.0405	43.9504	1.6429	−.7739
− 5.0	268.16	0.0037291	0.0287	62.0206	1.7925	−.6358
− 3.0	270.16	0.0037015	0.0246	72.3574	1.8594	−.5721
+ 2.0	275.16	0.0036342	0.0220	80.9088	1.9079	−.5316
8.0	281.16	0.0035567	0.0173	102.8898	2.0123	−.4365
13.00	286.16	0.0034945	0.0153	116.3394	2.0657	−.3908
15.00	288.16	0.0034703	0.0132	134.8479	2.1298	−.3298
18.00	291.16	0.0034345	0.0119	149.5792	2.1748	−.2892
20.00	293.16	0.0034111	0.0113	157.5214	2.1973	−.2697
23.00	296.16	0.0033766	0.0094	189.3609	2.2773	−.2011
32.00	305.16	0.003277	0.0074	240.5395	2.3812	−.1033
34.00	307.16	0.0032556	0.0068	261.7636	2.4179	−.0695
39.00	312.16	0.0032035	0.0056	317.8558	2.5022	+.0078
44.00	317.16	0.0031530	0.0048	370.8318	2.5691	+.0678
50.00	323.16	0.0030944	0.0041	434.1446	2.6376	+.1282

Table. 4

C$_3$=0.4326M   5,6 dimethyl benzotriazole

T°C	T°K	1/T	τ Sec	Kl^{2}mol^{-2}sec^{-1}	log K	log K/T
−15.00	258.16	0.0038736	0.0874	30.5681	.1.4852	−.9266
−11.00	262.16	0.0038145	0.0712	37.5232	1.5742	−.8442
− 1.0	272.16	0.0036743	0.0349	76.5516	1.8839	−.5508
5.0	278.16	0.0035951	0.0266	100.4381	2.0018	−.4424
8.0	281.16	0.0035567	0.0258	103.5521	2.0151	−.4337
10.0	283.16	0.0035316	0.0211	126.6186	2.1024	−.3495
13.0	286.16	0.0034945	0.0215	124.2629	2.0943	−.3622
17.0	290.16	0.0034464	0.0186	143.6372	2.1573	−.3053
20.0	293.16	0.0034111	0.0171	156.2370	2.1938	−.2733
23.0	296.16	0.0033766	0.0147	181.7451	2.2595	−.2120
26.0	299.16	0.0033427	0.0146	• 182.9894	2.2624	−.2134
28.0	301.16	0.0033205	0.0120	222.6378	2.3475	−.1311
30.0	303.16	0.0032986	0.0119	224.5087	2.3512	−.1304
33.0	306.16	0.0032663	0.0106	252.0428	2.4014	−.0844
40.0	313.16	0.0031933	0.0089	300.1858	2.4774	−.0184
43.0	316.16	0.0031630	0.0081	329.8337	2.5183	+.0183
46.0	319.16	0.0031332	0.0073	365.9799	2.5635	+.0594
48.0	321.16	0.0031137	0.0067	398.7542	2.6007	+.0939
50.0	323;16	0.0030944	0.0060	445.2756	2.6484	+.1392

Table 5

Thermodynamic parameters of 5.6 dimethyl benzotriazole.

Conc. mol/1	E$_a$ KJ/mol	log A	$\triangle$*H KJ/mol	$\triangle$*S J deg^{-1} mol^{-1}	$\triangle$*G$_{298}$ KJ/mol
0.530	25.675	6.785	23.245	-123.18	59.953
0.4850	26.757	6.959	24.491	-119.35	60.-57
0.4326	26.643	6.946	24.285	-119.88	60.00

The rate constant values (K = 30.5681 l^2 mol^{-2} Sec^{-1} for 5,6 dimethyl benzotriazole, K = 65.12 l^{2}mol^{-2} sec^{-1} for 1,2,3 benzotriazole) of these compounds also provide the same information, at a given temperature (-15°C). This could be understood if one considers

the mechanism of H-transfer in these compounds. Although we have said[2] that exchange of the H-atom occurs in a cyclic trimer we may use (X) and (Y) for discussion, because the mechanism remains the same.

(X)

(Y)
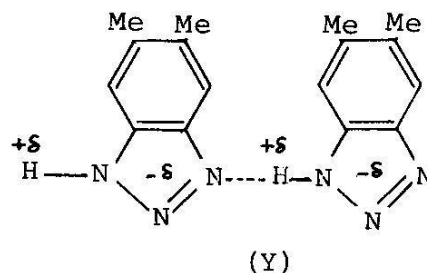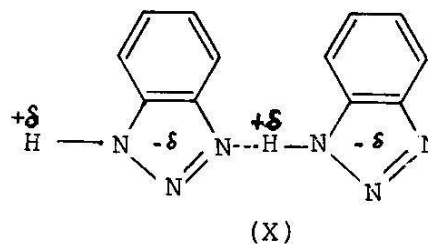
The substitution of two methyl groups in the benzene ring, increases the electrodensity in the heterocyclic ring consequently breaking of N-H bond in (Y) becomes more difficult than in (X), or in other words (Y) is less acidic than (X). If breaking the N-H bond is the rate determining step of proton transfer in these compounds one would expect a faster exchange in (X) than that in (Y). We have observed[2] that water catalyses the exchange rate in these systems.

The possibility of N-H bond breaking, being the rate determining step becomes more obvious if the mechanism of this catalysis is considered. The water molecules help in breaking N-H linkage through hydrogen bonding.

A loosely bound activated complex has a higher entropy ($\triangle$*S) value than a tightly bound one. The more positive value of $\triangle$*S = -120.8 J deg^{-1}mol^{-1} for 5,6 dimethyl benzotriazole than $\triangle$*S =-152.2566 J deg^{-1}mol-1 for 1,2,3 benzotriazole indicates that the former has a less ordered transition structure than the latter one. This could be attributed to overcrowding in the transition state caused by the bulky groups (Me) in 5,6 dimethyl benzotriazole.

Acknowledgement

References

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