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Proton NMR Spin – Lattice Relaxation Time in Some Bismaleimides

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Abstract: ***In this present work we have carried out proton NMR spin-lattice relaxation time ^1H T_1 measurements of some bismaleimides at 400MHz in DMSO using pulse sequences, and inversion-recovery experiment. This experiment uses two pulses, 180° and 90°, separated by a delay time τ which is varied. The present study, as a part of studying the effect of ring and side chain substitutions on the amides proton spin-lattice relaxation.^1H T_1 values of imide protons for model system of studied compounds appeared systematically correlation with the differences in type (direct, aromatic and aliphatic) and aliphatic chain length spacer link between two maleimide rings in the each studied compounds. ^1H T_1 value for imide protons of hydrazine bismaleimide BMI1 is 8.0790sec (which have direct linking between two maleimides rings), were increase up to ethylene bismaleimide BMI2is 8.2233sec and propylene bismaleimide BMI3 is9.5217sec (which have ethylene and propylene chain spacer respectively), then decrease ^1H T_1values in hexamethylenebismaleimideBMI4 and octamethylenebismaleimide BMI5 become7.7905 and 7.5020sec respectively. The comparison between the aromatic linking, the values of ^1H $T_1$for imide protons in phenyl bismaleimide BMI6 and diphenylsulphonbismaleimideBMI7(which have aromatic link spacer) are 7.2134 and 5.7707 sec respectively. It is less than the values in the event that the aliphatic chain link or directly linked. The effect of temperature on the relaxation timeT_1 has been study.***

Keywords: Spin-lattice relaxation timeT_1, bismaleimides, effect of ring and side chain substitutions.

1. Introduction

Nuclear magnetic resonance (NMR) is widely used for monitoringthe reorientational and translational dynamics of molecules[1]. Spin-lattice relaxation times T_1 value can be used as an aid in spectral assignment as in ^{13}Cspectrum[2]. NMR relaxation properties ofmetabolite nuclei are the key factors influencing the accuracy ofmetabolite quantification [3]. Nuclear magnetic relaxation properties provide important information on the dynamic properties of fluids [4]. Many studies of spin –lattice relaxation time in the laboratory T_1, of different biopolymers have been reported in the literature [5-7]. The measurement of proton T1 offers an excellent way of probing the molecular motions characterized [8]. Information about local molecular mobility is available from spin-lattice and spin-spin relaxation rates [9]. As general rule the intensity of a ^{13}C signal will be inversely proportional to its T_1 value unlike ^{13}C, the ^{1}H spectra do not reflected by T_1 values because of fast relaxation of ^{1}H. However, chemical shifts and coupling constants are independent on molecular reorientation, not like T_1 values. T_1 values act as powerful sources of information on both intermolecular and intramolecular motions. This information can be used in study of segmental motion, association and complexation.The interpretation of spin relaxation rates is generally difficultbecause they depend on various mechanisms such as inter- and intra-molecular dipolar interactions[10].

2. Measurement of T_1 for Studied Compounds

Spin-lattice relaxation times T_1 for proton of the studied bismaleimides BMI1- BMI7 measured at 400MHz in DMSO at 26°C. ^{1}H T_1 values were determined using pulse sequences, and most common one being the so-called inversion-recovery experiment uses two pulses, 180° and 90°[11], separated by a delay time τ which is varied. For each delay a certain number of free induction decay FIDs are accumulated. The results are a series of spectra in which the individual signals have different intensities. Figures(4 and 5) shows some results of an inversion-recovery experiment carried out of studied bismaleimides BMI1and BMI5 respectively.

Each proton behaves differently, because it has its individual relaxation time T_1, depending on the delay signals may be negative, positive, or have zero intensity. The T_1 values can be computed using spectrometer software or using Bloch equation:

$$M_z = M_z^o\ [1 - 2\ exp(-t/T_1)] \quad \ldots\ldots\ (1)$$

at t=o immediately after the 180° pulse M_z will be equal -M_z^o, and after t= ∞ or > 5T, $M_z = M_z^o$. $M_z^o$is the magnetization in z-direction at equilibrium.

When $M_z$passes through zero, at t_o, equation (1) becomes,

$$0 = M_z^o\ [1 - 2\ exp(-t/T_1)] \quad \ldots\ldots\ (2)$$

and

$$T_1 = \frac{t_o}{2.303 \log 2} = \frac{t_o}{0.693} \quad \ldots\ldots\ (3)$$

Therefore, T_1 can be determined from bin owing to value for any singl line in the spectrum. In a second method, in practice, a 180° pulse is applied and then after a delay of τ (time) a second 90° pulse is applied which converts the magnetization onto the –y` axis, where it can be detected, since the receiver is on the y` axis.

3. Results and Discussion

In this present work we have carried out ^{1}H T_1 measurements for studied bismaleimides BMI1- BMI7 at 400 MHz in DMSO at 26°C. The values of chemical shift, time period and T_1 relaxation time for the various proton signals are shown in Table 1. Before the relaxation time measurements, oxygen should be removed[12] through repeatedly freezing the contents of a specially constructed

NMR tube by dipping it in liquid nitrogen, evacuating the tube, and then thawing.

^{1}H T_1 values of imide protons for model system of studied compounds appeared systematically correlated with the differences in type (direct, aromatic and aliphatic) and aliphatic chain length spacer link between two maleimides rings. ^{1}H T_1 value for imide protons of hydrazine bismaleimide BMI1is 8.0790sec (which it has direct linking between two maleimides rings) increases up to ethylene bismaleimideBMI2is 8.2233sec and propylene bismaleimideBMI3is 9.5217sec, then decreases in hexamethylenebismaleimideBMI4 and octamethylenebismaleimideBMI5 become 7.7905 and 7.5020sec respectively. This behaves can be explain in term of increasing reorientational motion of the two rings, which leads to decrease of the correlation time of the motion due to presence of the spacer. This relationship is illustrated in Figure 2. In bismaleimidesBMI4 and BMI5, the molecular weight become dominated effect on reorientational motion which leads to increase the correlation time due to that the correlation time is strongly dependent on molecular weight but also is a function of the shape of the molecule. The relaxation process is caused by fluctuating local magnetic fields created by neighboring chemical environments. These fluctuations are a result of molecular motion. In liquids with spin ½ nuclei, the major contributors to relaxation are dipolar effects and chemical shift anisotropy (CSA). The dipolar effects, as the name implies, are results of interactions between two nuclei with magnetic dipoles. CSA is somewhat more complicated due to the fact that the chemical shift of a given nucleus is dependent on the orientation of that nucleus with the external field[13] .

By comparison between the presence of aromatic space, the values of ^{1}H $T_1$for imide proton in phenyl bismaleimideBMI6 and diphenyl sulphonbis maleimideBMI7(which have aromatic link spacer) are 7.2134 and 5.7707sec respectively. It is less than the value in the event that the aliphatic chain link or directly linked, that's due to the fact is the molecules with a rigid central core (such as a ring system) and a freely that moving side chain may exhibit significant differences in the mobility of the protons of ring system as compared to the side chain. These are reflected in their corresponding relaxation rates. This relationship is illustrated in Figure 3.

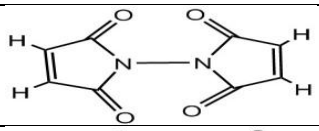
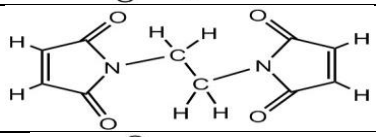
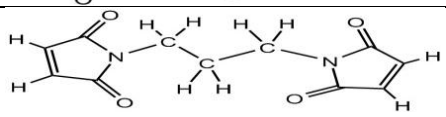
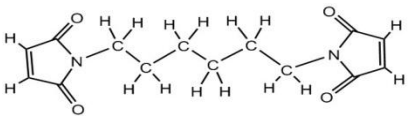
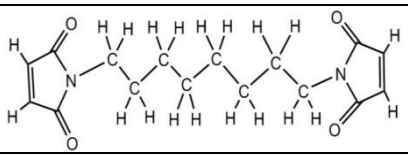
^{1}H T_1 for aromatic proton in phenyl bismaleimideBMI6 and diphenylsulphonbismaleimideBMI7 are 2.3083 and (2.0197 and 1.5869) respectively, were longer than 0.7213, (0.7934 and 0.7213), (0.7905, 0.5770 and 0.504), (7.5020, 06492 and 0.5049)sec^{1}H T_1 for aliphatic proton in compounds BMI2, BMI3, BMI4 and BMI5 respectively.

The rate of molecular tumbling increases with temperature and with reducing viscosity of the solvent, therefore, the temperature dependences of the ^{1}H NMR relaxation times T_1 value [14-16], therefore, to study the effect of temperature on the chemical shift and relaxation time, the relaxation time measurements were carried out for compounds BMI1, BMI3 and BMI6 at a temperature of 49 °C. The results showed high values of relaxation time dramatically while maintaining the same order for the increase in the value. Table 2 listed the chemical shift, time period τ and ^{1}H T_1relaxation time for bismaleimidesBMI1, BMI3, and BMI6 at 49 °C and 400MHz (DMSO) and figure 4 shows the relationship for imide protons ^{1}H T_1 values at 49^{o}C .

4. Acknowledgements

The authors greatly acknowledge the support from Technical University (TU) Braunschweig - Organic Chemistry Institute, Braunschweig, Germany.

Table 1: Protons chemical shift, time period and T1 relaxation time for the protons in studied bismaleimidesBMI1-BMI7 measured by 400MHz, (DMSO).

No.	*Compound symbol*	*Structure*	*Chemical shift (ppm)*	*τ (sec)*	*Relaxation time T1 (sec)*
1	**BMI1**		7.408	5.60	8.0790
2	**BMI2**		7.020	5.70	8.2233
			3.550	0.50	0.7213
3	**BMI3**		7.025	6.60	9.5217
			3.260	0.55	0.7934
			1.790	0.50	0.7213
4	**BMI4**		7.010	5.40	7.7905
			3.130	0.40	0.5770
			1.450	0.40	0.5770
			1.220	0.40	0.5770
5	**BMI5**		7.001	5.20	7.5020
			3.370	0.45	0.6492
			1.460	0.35	0.5049
			1.200	0.35	0.5049

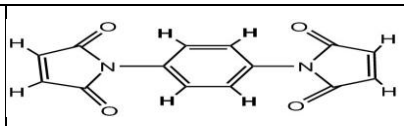
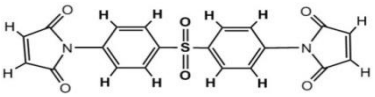
6	**BMI6**		7.460	1.60	2.3083
			7.240	5.00	7.2134
7	**BMI7**		8.125	1.10	1.5869
			7.643	1.40	2.0197
			7.240	4.00	5.7707

Table 2: Protons chemical shift and T1 relaxation time of bismaleimidesBMI1, BM3 and BMI6 at 26°C and 49 °C, measured by 400MHz, (DMSO)

No.	Compound symbol	At 26 °C		At 49 °C	
		Chemical shift (ppm)	T1 relaxation time(sec)	Chemical shift(ppm)	T1 relaxation time(sec)
1	BMI1	7.4180	8.0790	7.3800	13.7056
2	BMI3	7.0100	9.5217	6.8000	16.4467
		3.3850	0.7934	3.4000	1.2984
		1.773	0.7213	1.8000	1.1541
3	BMI6	7.4630	2.3083	7.4800	3.1739
		7.2100	7.2134	7.1900	10.9644

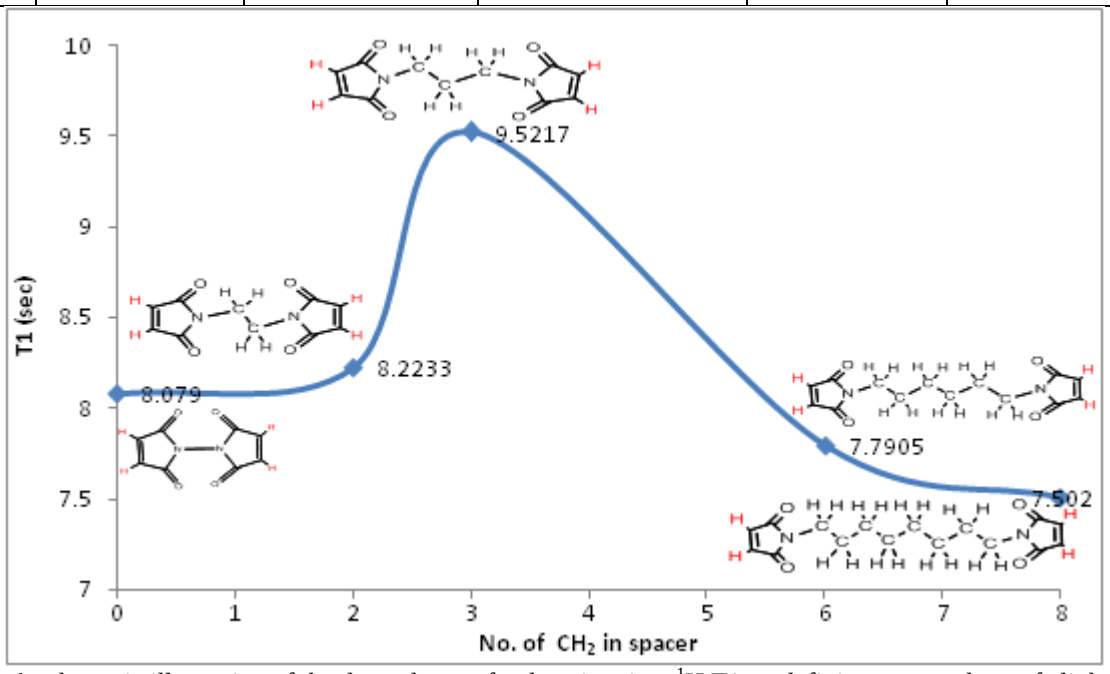


Figure 1: A schematic illustration of the dependence of relaxation time ^{1}H T1on olefinic proton to long of aliphatic chain spacer inbismaleimidesBMI1-BMI5.

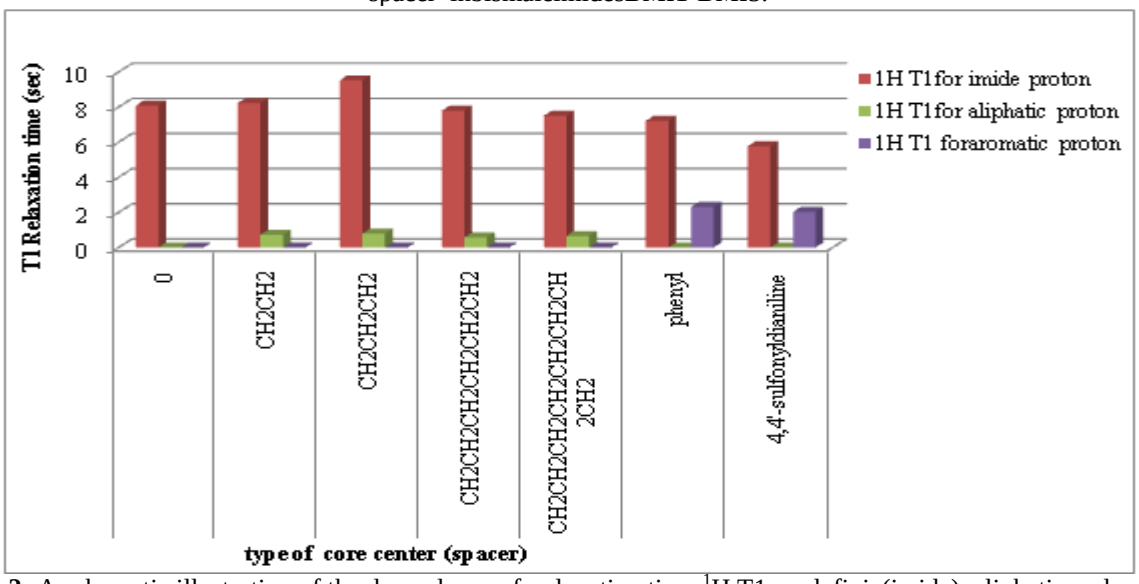


Figure 2: A schematic illustration of the dependence of relaxation time ^{1}H T1on olefinic(imide), aliphatic and aromatic protons to type and long of chain spacer in studied bismaleimides BMI1-BMI7.

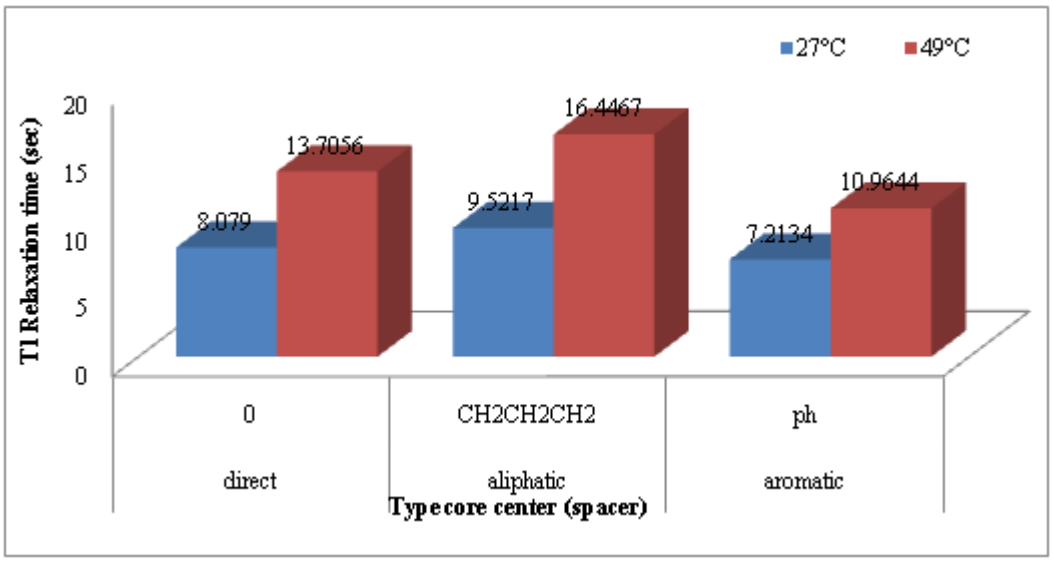


Figure 3: A schematic illustration of the dependence of relaxation time ^{1}H T1on olefinic(imide), aliphatic and aromatic protons to temperature in bismaleimidesBMI1, BMI3 and BMI7.

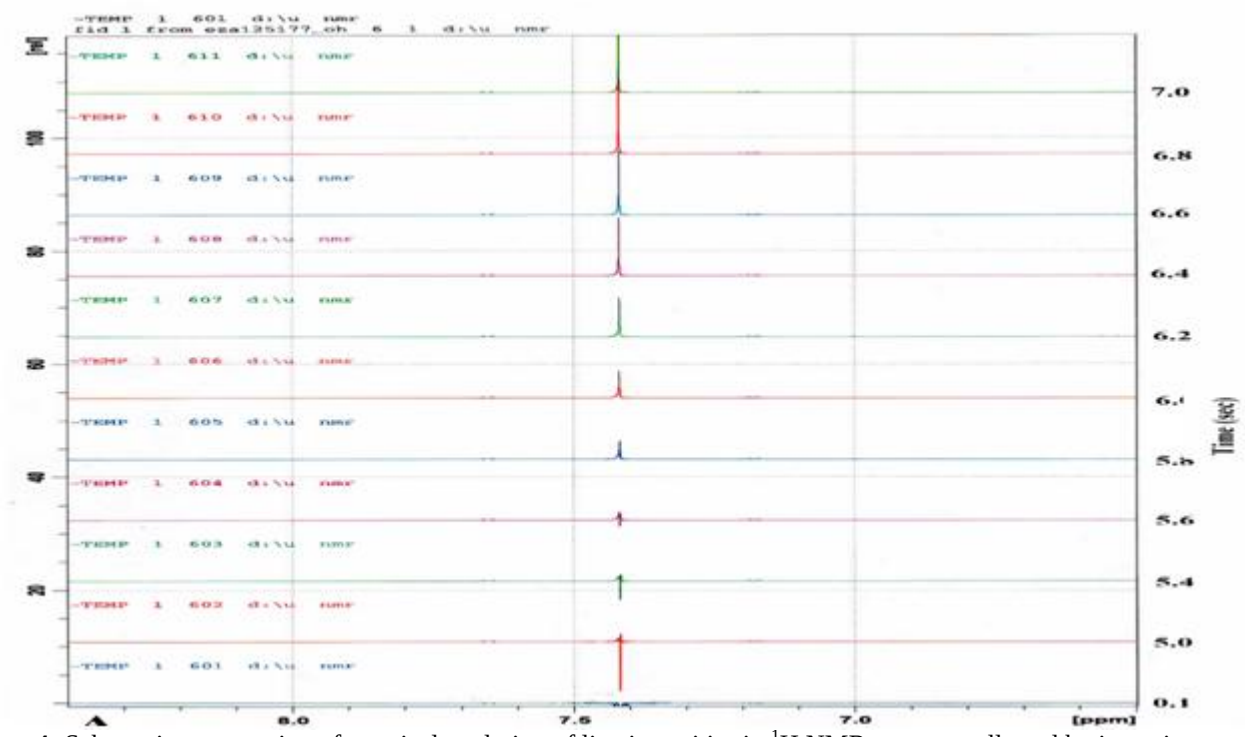


Figure 4: Schematic presentation of a typical evolution of line intensities in ^{1}H NMR spectra, collected by inversion recovery experiments at different values of τ (at 400 MHz in DMSO, at 26°C)of bismaleimideBMI1.

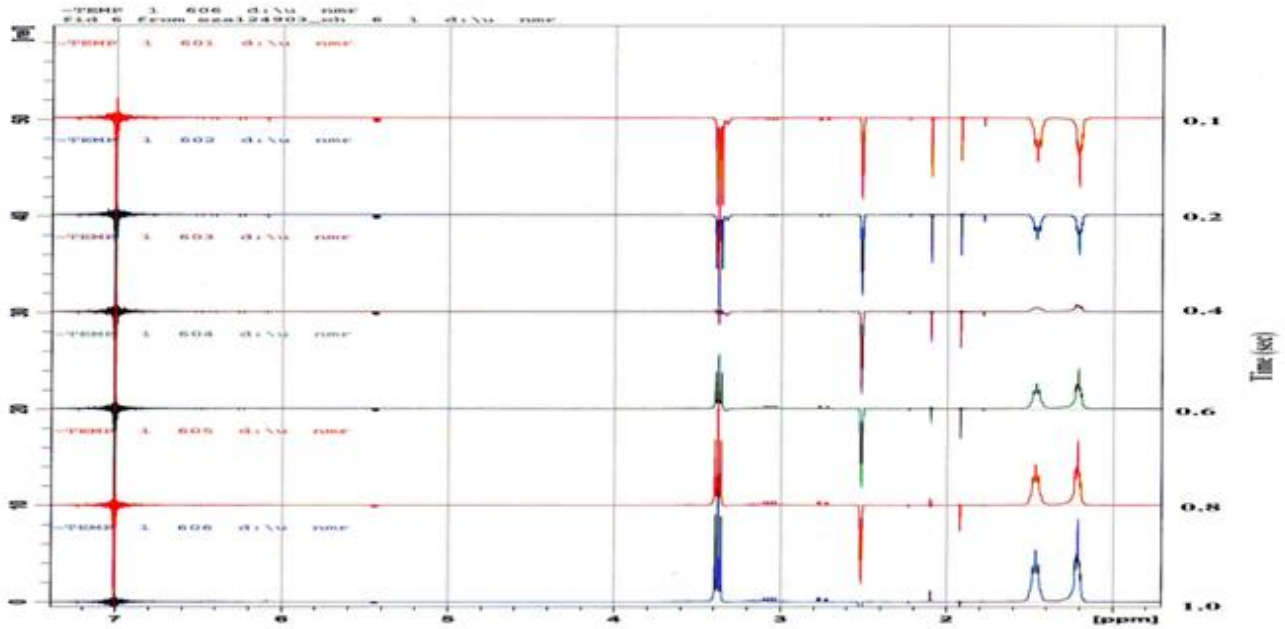


Figure 5: Schematic presentation of a typical evolution of line intensities in ^{1}H NMR spectra, collected by inversion recovery experiments at different values of τ (at 400 MHz in DMSO at 26°C) of bismaleimideBMI5.

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