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Determination of isomer ratio of TDI using NMR technique

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ABSTRACT

Commercially available toluene diisocyanate (TDI) contains 2, 4-and 2, 6-isomer of TDI. Successful attempts have been made to determine the 2, 4-and 2, 6- isomer ratio of TDI using proton NMR technique at 300 MHz. The percentage of 2, 4-and 2, 6-isomer of TDI has been calculated based on the methyl protons as well as aromatic protons. The analysis data indicate that the value of 2, 4- & 2, 6 isomers are in ratio of 80:20 having ± 0.5 % tolerance. Further, the developed technique does not require any reference sample as other methods.

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KEYWORDS

Composite propellant;
TDI;
Isomer ratio;
NMR.

INTRODUCTION

Toluene diisocyanates (TDI) are rapidly gaining importance as chemical intermediates, because of their use in solid rocket propellants, polyurethane foams and elastomers^[1]. TDI exists in two isomeric forms and the two isomers differ mainly in two ways. Firstly, the relative reaction rates of the different isocyanate groups on each molecule differs considerably^[2]. The reactivity of the *ortho* position in 2,4 isomer is approximately 12% of the reactivity of the *para* position due to the steric hindrance caused by the methyl group. However, when the reaction temperature approaches 100°C, steric hindrance effects are overcome and both the positions react at nearly the same rate. In comparison, the NCO groups on 2, 6-TDI have equal reactivities though the reactivity of the second isocyanate group drops by a factor of around 3 after the first group reacts. The second way in which the two isomers differ is that the 2, 6-isomer is symmetric as compared to 2, 4-isomer and therefore is expected to form hard segments with better packing characteristics. As the relative proportions

of the 2, 4- and 2, 6-isomers are known to affect the curing reaction rate, which in turn, affects the pot life of the propellant slurry and mechanical properties of cured propellant, therefore a suitable method for analyzing these mixtures is extremely important.

The conventional chemical determination of isocyanates^[3-6] by reaction with excess di-n-butylamine followed by acidimetric titration of the unreacted amine is suitable for determining total isocyanates. However, this method fails to distinguish between the isomers. Literature survey reveals that different methods have been reported for the determination of isomer ratio of TDI. The most common method for the determination of isomer ratio is FTIR method^[7,8] which is based on the quantitative measurement of absorption bands arising from out-of-plane C-H deformation vibrations of the aromatic ring at 810cm⁻¹ and 782cm⁻¹. Furthermore, another important method for the determination of isomer ratio of TDI is gas chromatography technique by marcali et al in which TDI is hydrolyzed to the corresponding diamine, diazotized, coupled to N-1-naphthylethylene diamine^[9] and later on the above method was modified

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by Rando^[10] and Meddle et al^[11]. Another chromatographic methods used for the determination of isomer ratio of TDI are liquid chromatography and high performance liquid chromatography^[12-17] using derivatized procedure as well as impregnated paper tape technique^[18]. In continuation to determination of isomer ratio of TDI, a coated piezo electric crystal^[19,20] method has also been employed to detect TDI in air.

However, method based on FT-IR, HPLC, Freezing point, Dielectric constant have disadvantages as FT-IR method requires dry solvents as well as individual pure isomers of TDI. HPLC method requires derivative of TDI otherwise separation in column is difficult. Also, freezing point and dielectric constant methods require large quantity of TDI for calibration.

In continuation to this work further, the isomer ratio of TDI was determined by platten^[21] using NMR technique taking in consideration of resonance of methyl protons in hexa fluoro benzene. However, this method describes the determination of isomer ratio of TDI based on methyl proton at 60 MHz. Further to this, TDI contain both aliphatic and aromatic protons and platten study reveals that determination of isomer ratio of TDI was based on methyl protons only and it is also clear from the literature survey that determination of isomer ratio of TDI based on aliphatic and aromatic protons has not been reported. Therefore, a successful attempt has been carried out to determine isomer ratio of TDI taking full consideration of both methyl and aromatic protons using NMR technique at 300 MHz to have better resolution.

In the following section, we report the method of determination of isomer ratio of TDI using NMR technique at 300 MHz taking full consideration of both methyl and aromatic protons.

EXPERIMENTAL

Material

Toluene diisocyanate, purity 99.53 %, used for the analysis is a mixture of 2, 4 and 2, 6- isomers and procured from Bayer, Germany BSAF-U.S.A., DOW-U.S.A., Mitsui chemicals-Japan and Konnate-Korea.

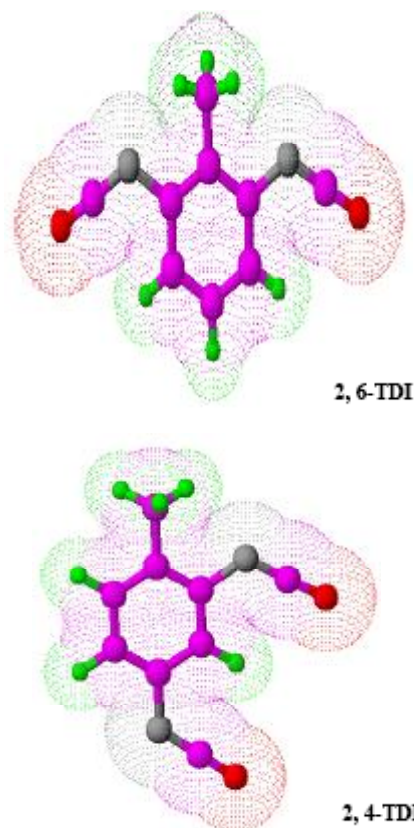
Measurements

Proton NMR analysis was carried out on 300 MHz

instrument using CDCl_3 as a solvent and tetra methyl silane (TMS) as an internal standard.

RESULTS AND DISCUSSION

In a molecule of TDI, π electrons are delocalized cyclically over the aromatic ring. These loops of electron are induced to circulate in the presence of the applied field, B_0 , producing a substantial electric current, called the ring current.



The induced magnetic field is diamagnetic (opposing B_0) in the center of the ring, while the returning flux outside the ring is paramagnetic. So protons around the periphery of the ring experience an augmented magnetic field and consequently come to resonance at higher values than would otherwise be so. Protons held above or below the plane of the ring resonate at low δ values. In general greater the shielding, lower the precessional frequency or lower δ value (upfield) and higher the deshielding, higher the δ values (downfield).

Calculation of isomer ratio from peak area of methyl protons

TABLE 1: Chemical shift value of TDI

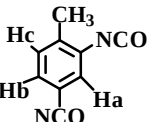
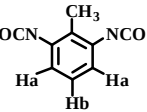
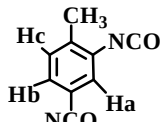
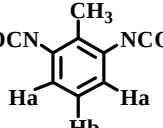
Sl. no	Isomer	Proton	Chemical shift	Multiplet	Coupling constant
1		Methyl	$\delta = 2.300$	s	-
		H _a	$\delta = 6.798$	d	$J_{ab} = 2.1$ Hz
		H _b	$\delta = 6.836$	dd	$J_{bc} = 8.1$ Hz
		H _c	$\delta = 7.112$	d	$J_{cb} = 8.1$ Hz
2		Methyl	$\delta = 1.600$	s	-
		H _a	$\delta = 6.940$	d	$J_{ab} = 8.1$ Hz
		H _b	$\delta = 7.247$	s	-

TABLE 2: Isomer ratio from methyl proton peak area

Sl.no	Isomer	Proton	Peak area	Total area (2,4+2,6)	Isomer content
1		Methyl	45.15	56.68	79.66 %
2		Methyl	11.53	56.68	20.34 %

The methyl group in 2, 6-isomer resonate at δ 1.6 whereas in 2, 4-isomer methyl group resonate at δ 2.3. The change in chemical shift in 2, 6-isomer is because of the methyl group is flanked by two isocyanate groups and more electron density (electron donation from both isocyanate group) around methyl protons which shields the hydrogen nucleus from the influence of the applied field B_0 , there by causing the methyl proton resonate at low δ value compared to 2,4-isomer where the methyl proton is comparatively less shielded. Since methyl group in 2, 4-isomer and 2, 6-isomer resonate at different δ values, therefore, it is possible to determine the isomer ratio by measuring the peak area from the NMR spectrum (Appendix-1) and accordingly TABLE 1 shows the peak assignment and chemical shift values of TDI.

Peak area at δ 2.3 is 45.15 (due to 2, 4-isomer methyl proton)

Peak area at δ 1.6 is 11.53 (due to 2, 6-isomer methyl proton)

Total peak area is 56.68 (TABLE 2)

Percentage of 2, 4 isomer = $45.15 \times 100 / 56.68 = 79.66 \%$

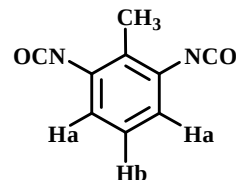
Percentage of 2, 6 isomer = $11.53 \times 100 / 56.68 = 20.34 \%$

Calculation of isomer ratio from peak area of aromatic protons

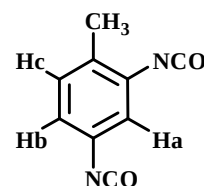
Isomer ratio can also be determined by measuring peak area of aromatic protons because in 2, 4 and 2,

6-isomer protons resonate at different δ values because of electronic effect of methyl and isocyanate group.

2, 6-Toluene diisocyanate (2-methyl-1, 3-phenyl endediisocyanate)



It is clear from the NMR spectrum that proton H_b appears as a broad singlet at δ 7.247 with peak area equal to 6.51. where as proton H_a couples with proton H_b and appears as a doublet centered at δ 6.940 with peak area equal to 12.96 and coupling constant $J_{ab} = 8.1$ Hz, a typical value of ortho coupling. A low δ value for proton Ha is due to electron donation from isocyanate group which shields the proton from the influence of external magnetic field compared to H_b proton where it is meta to both isocyanate groups. Thus, total peak area of 2, 6-TDI is $6.51 + 12.96 = 19.47$



2,4-Toluene diisocyanate (4-methyl-1, 3-phenyl endediisocyanate)

The NMR spectrum clearly reveals that proton H_a appears as a doublet centered at δ 6.798 with coupling constant $J_{ab} = 2.1$ Hz, a typical value of meta coupling. Proton H_b appears as doublet of doublet centered at δ 6.836. Proton H_b coupled with proton H_c gives a doublet with coupling constant $J_{bc} = 8.1$ Hz. Also, proton H_b coupled with proton H_a gives a doublet with coupling constant $J_{ba} = 2.1$ Hz. Proton H_c also appears as a doublet centered at δ 7.112 because of its coupling with proton H_b having coupling constant value $J_{cb} = 8.1$ Hz. The position of each peak is in accordance with electronic effect of methyl and isocyanate groups. Peak area of proton H_a and H_b is 47.79. Peak area of proton H_c is 32.74 (TABLE 3).

Total peak area of 2, 4-TDI is $47.79 + 32.74 = 80.53$

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TABLE 3: Isomer ratio from aromatic proton peak area

Sl.no	Isomer	Proton	Peak area	Total area (2,4+2,6)	Isomer content
1		H _a +H _b H _c	47.79 32.74	100	80.53 %
2		H _a H _b	12.96 6.51	100	19.47 %

TABLE 4: Isomer ratio of TDI based on methyl and aromatic proton

Sl.no	Source	Methyl proton		Aromatic proton	
		%2,4	%2,6	%2,4	%2,6
1	Bayer, Germany	79.66	20.34	80.53	19.47
2	BASF-USA	80.12	19.88	80.27	19.73
3	DOW-USA	80.34	19.66	79.82	20.18
4	Mitsui chemicals/Japan	79.42	20.58	79.95	20.05
5	Konnate/Korea	79.63	20.37	80.41	19.59

Calculation of isomer ratio

Total peak area 2, 6-TDI + 2, 4-TDI = 19.47 + 80.53 = 100.0

Percentage of 2, 4-isomer = $80.53 \times 100/100 = 80.53\%$

Percentage of 2, 6-isomer = $19.47 \times 100/100 = 19.47\%$

Further to this, TDI samples from different sources Viz; Bayer-Germany, BASF-USA, DOW-USA and Mitsui chemicals-Japan and Konnate-Korea were also analyzed using the developed technique and results obtained are presented in the TABLE 4. It is clear from the TABLE that percentage of isomer ratios of 2,4 and 2,6-TDI based on methyl and aromatic protons are in agreement with the specified values which further supports the authenticity of the developed technique.

CONCLUSION

Determination of isomer ratio of TDI using NMR technique at 300 MHz has been carried out successfully. Result obtained using this technique shows that $\pm 0.5\%$ variation. This technique not only takes less time, but also does not require any reference sample as other methods require. Also, the technique is more reliable, rapid and accurate.

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