

A Simple Method for the Preparation of 2,4,6-trichloroborazine and Evaluation of ^1H -NMR Spectra

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ABSTRACT: The compound 2,3,6-trichloroborazine (TCB) is known as a valuable precursor to prepare boron nitride and various derivatives of borazine. Difficulties in the preparation of TCB via conventional methods on the one hand, and its importance for material science, on the other hand, were our motivations to modify Brown's method for TCB synthesis. So far, all reports on the synthesis procedure of TCB are based on the use of gaseous BCl_3 with NH_4Cl powder at 110-130 °C in chlorobenzene requiring complicated low-temperature equipment such as a cold finger condenser, and dry ice-acetone reflux condenser to retain BCl_3 gas in the reaction flask. According to our study, using BCl_3 solution in *n*-hexane was more convenient than using gaseous BCl_3 . The reaction of BCl_3 solution with NH_4Cl was carried out without loss of BCl_3 . Furthermore, the reduction in the reflux temperature from 130 °C in some previous studies to 86 °C in our study, was a valuable advantage, leading to the release of the coordinated BCl_3 from the adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$ gradually and the prevention of thermal decomposition of TCB, unwanted polymerization reactions and the formation of undesirable products, resulting in the increased reaction yield. TCB was fully characterized by ATR-FT-IR, ^{11}B -, ^{14}N -, and ^1H -NMR spectroscopic methods. ^1H -NMR spectra of TCB were performed for the first time at various temperatures to elucidate the quadrupole effect of nitrogen, leading to the observation of the proton resonance splitting of the ^{14}N -H bond by coupling with the ^{14}N quadrupole nucleus. The broad peak observed at room temperature was clearly split into a triplet at 100 °C due to the long T_{qN} and fast molecular motion of TCB molecules. The ^{14}N -NMR spectrum was also shown for the first time as a broad signal at $\delta = -271.3$ ppm ($h_{1/2} = 186$ Hz).

KEYWORDS: Borazine derivatives; Adduct complex; NMR-Spectroscopy; Quadrupole effect; Boron trichloride.

INTRODUCTION

Due to the excellent mechanical and dielectric properties, in addition to thermal and chemical stability, boron nitride materials (BN) are used in lubricants, hydrogen storage

materials, electronics, aerospace, sensors, and many other high - tech industries [1-4]. The hexagonal boron nitride materials (h-BN) are one of the most important boron

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1021-9986/2022/4/1232-1239

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nitrides, due to the sp^2 covalent bond in the h-BN layer. Hence, the synthesis methods of h-BN have been improved greatly since 1999, mainly including high-temperature synthesis, vapor deposition, and liquid precursor methods. The structure and properties of h-BN materials can be controlled through precursor design in the liquid precursor method. This feature has led researchers to turn to the precursor design methods as the most remarkable ones for preparing BN ceramic fibers, films, and coatings [5]. Therefore, the design and preparation of starting material is a key research topic for the synthesis of h-BN.

Borazine ($B_3N_3H_6$) and some of its derivatives such as 2,4,6-trichloroborazine and alkyl amine borazine [6] are the proper and efficient precursors to prepare h-BN materials. Borazine is a six-membered heterocyclic compound with boron and nitrogen atoms alternating, which was synthesized for the first time by A. Stock and E. Pohland in 1926 [7, 8]. Borazine is also called “inorganic benzene” due to its similarity to benzene (C_6H_6) in physical properties, in addition to the molecular structure and comparable bond lengths (B–N 1.44 Å in $B_3N_3H_6$, and C–C 1.40 in C_6H_6) [7, 9]. Although borazine shows π -bonding characteristics, its aromaticity is less than benzene [7]. Borazine can be utilized for the preparation of BN materials, polymers, and ceramics [7]. Numerous derivatives of $B_3N_3H_6$ with the common name borazine are known.

The results of density functional theory (DFT) studies on borazine-like structures, $(B \text{ or } Al)_3(N \text{ or } P)_6(H \text{ or } CH_3)_9$, by K. Harismah et al in 2017 showed that the formation of $B_3N_3H_9$ is more favorable than the others [10]. Based on the calculated molecular orbitals energies, the mentioned borazine-like structures could be all considered semi-conductors and applied in the electronic industry [10]. According to the ab initio calculations performed by H.A. Dabbagh et al in 2014, the hydrogen storage capacity of the Borazine-Melamine Polymer (BMP) was calculated at about 6.49 wt%, and the maximum number of H_2 -molecules, adsorbed by the BMP building block were about ten [11]. The interaction of ions (Li^+ , Na^+ , K^+ , F^- , Cl^- and Br^-) with borazine ring as the π -system in borazine complexes has theoretically been investigated from NMR point of view and indicated that the electronic effects have the dominant role for determination of the hydrogen shielding. The B–H and N–H shieldings increase and decrease in anion- π and cation- π complexes, respectively [12]. The reactivity of 2,4,6-trichloroborazine (TCB)

and some of its alkyl amine derivatives was investigated by Q.Z. Han et al in 2013 by means of DFT [5]. It could be shown that the stability of NMe_2 derivatives is higher than that of $NHMe$. Considering the results of their work can be profitable for the selection of the reaction conditions and controlling the shape of h-BN in the current synthesis methods [5]. The preparation of boron nitride was performed using trichloroborazine [13] and dichloroborazine [14] as the starting materials and the reaction condition and the product yield was as well discussed [13]. Recently, it has been also found that the h-BN prepared by TCB has some advantages of low sintering temperature and high purity [5]. W. Auwärter et al, analyzed the molecular structure, and bonding energy of the h-BN single crystals, prepared from TCB using DFT B3LYP/6-31G (D, P) basis set in 2004 [15] and showed that the preparation and modification of TCB as the h-BN precursor, is an attractive issue for the researchers in the world.

As mentioned above, among the derivatives of borazine, 2,4,6-trichloroborazine is known as an appropriate precursor for the preparation of other borazine derivatives, and boron nitride fibers with unique properties [16, 17]. The white solid of TCB is extremely sensitive to moisture and hydrolyzes very quickly in the presence of humidity and oxygen releasing boric acid, ammonia, and HCl gas [18]. Due to the presence of chlorine groups on boron atoms, TCB is active toward the nucleophilic substitution reactions on boron atoms, to prepare the new derivatives. In recent years, some derivatives of borazine were synthesized utilizing TCB and various reagents, such as Grignard, organolithium compounds, and amines [18-20]. Furthermore, borazyl and fluorinated borazylcarbenes were investigated in comparison to those of phenylcarbene [21]. The synthesis of TCB, was first carried out in 1940 by Wiberg and Bolz, by thermal decomposition of the addition compound of borazine and hydrogen chloride $B_3N_3H_6 \cdot 3HCl$ [22]. The more convenient method was introduced by Brown and Laubengayer in 1955, in which 2,4,6-trichloroborazine (TCB) was prepared by refluxing a mixture of chlorobenzene and ammonium chloride in the presence of boron trichloride vapour with a yield of 36% [23]. However, this approach needed low-temperature equipment such as a cold finger condenser and dry ice-acetone reflux condenser to liquefy BCl_3 gas (b.p. 12.5 °C) in the reaction flask. They also reported that 2,4,6-trichloroborazine undergoes slow irreversible thermal

decomposition above 100 °C with the evolution of hydrogen chloride and the formation of non-volatile solids [23]. It means that the reaction should be performed under 100 °C. In 1967, Rothgery and Hohnsted prepared TCB by bubbling gaseous BCl₃ into the solution of chlorobenzene and acetonitrile followed by the reaction of the obtained acetonitrile-boron trichloride adduct with NH₄Cl, leading to a 57% increase in the yield [24]. However, the reaction temperature in chlorobenzene was 130 °C, which is responsible for the likely thermal decomposition of TCB. In accordance with the patent published in 1987 by Riccitiello et al., [25] TCB was synthesized utilizing gaseous BCl₃ and NH₃ in aprotic solvents at the temperature range of 100–150 °C with a yield of just about 40%, because, in parallel with the main reaction, ammonia also reacts with produced HCl to form NH₄Cl leading to reduce the reaction yield. However, this method was set aside due to difficulty in controlling the gaseous reactants and low yield. In 1996, Zakharkin and Olshevskaya [26] used an excessive amount of BCl₃ gas to react with the suspension of NH₄Cl in chlorobenzene at 110–120 °C. The reaction efficiency was improved to 89%. However, complicated low-temperature equipment was in turn required and the loss of BCl₃ gas was relatively high during the liquefying process. Also, in 1997 Nöth and Sachdev applied ¹¹B-NMR spectroscopy in order to monitor the reaction between BCl₃ and NH₄Cl. The proposed mechanism based on the online ¹¹B-NMR spectra showed the formation of some polymeric intermediates leading to a decrease in the reaction yield. Therefore, a twofold excess of BCl₃ gas was necessary to prevent or suppress competing reactions and achieve a high yield [27]. They also prepared TCB from bis(trimethylsilyl)amine HN(SiMe₃)₂ in place of NH₄Cl in 96% yield. This method was not widely used because of the expensive price of bis(trimethylsilyl)amine compared to NH₄Cl. In the last publication on the synthesis of TCB in 2010, Deng et al. reported on the use of boron trichloride-dimethyl sulfide complex [(CH₃)₂S·BCl₃] with NH₄Cl with a yield of about 65–70%. They also had to use low-temperature equipment [28]. However, efforts to optimize and simplify TCB synthesis have continued since 1940 and over eighty years after the synthesis of TCB, indicating the importance of valuable 2,4,6-trichloroborazine.

Difficulties in the preparation of TCB, such as the need to use complicated low-temperature equipment, working with harmful gaseous BCl₃, and low yield, led us to modify

Brown's method for TCB synthesis. In the present study, we used the solution of BCl₃ in n-hexane (1.0 mol/L) and acetonitrile to obtain a boron trichloride-acetonitrile complex [CH₃CN·BCl₃]. TCB was synthesized in high yield from the reaction of the adduct complex with ammonium chloride at a reduced reflux temperature (86 °C) to prevent the thermal decomposition of TCB. We also elucidated why the expected triplet splitting for ¹⁴N-H protons in TCB cannot be observed under normal conditions.

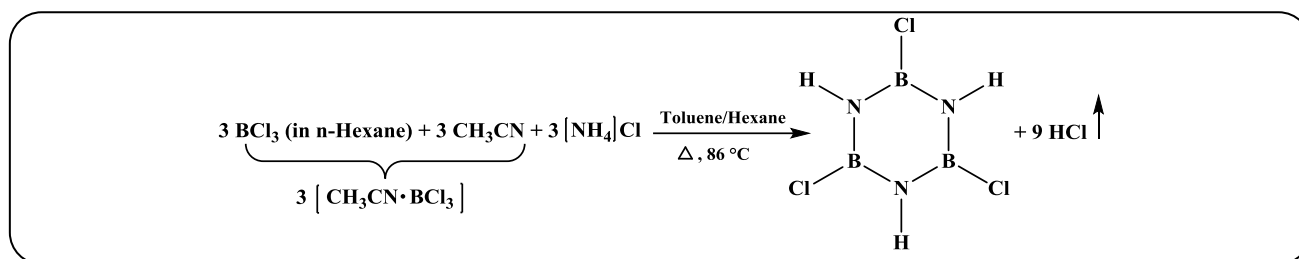
EXPERIMENTAL SECTION

Materials and General Procedures

Toluene and acetonitrile were purified and dried, using standard methods [29]. BCl₃ solution in n-hexane (1.0 mol/L) was purchased from Sigma-Aldrich. Ammonium chloride was dried using a silicone oil bath at 110 °C under vacuum for 10 hours. All experiments were carried out under an argon gas atmosphere, using the standard Schlenk technique. The ¹H-, ¹¹B-, and ¹⁴N-NMR spectra were recorded with a Bruker AVANCE AQS-300 MHz spectrometer. Chemical shifts (δ) for proton, boron, and nitrogen were reported relative to the internal standards tetramethylsilane (TMS, (CH₃)₄Si), boron trifluoride diethyl etherate complex [BF₃·O(C₂H₅)₂] and nitromethane (CH₃NO₂), respectively. The attenuated total reflectance spectrum was recorded on a Bruker Vector 22 ATR-FT-IR spectrometer equipped with a ZnSe single crystal spectrometer in the range of 600–4000 cm⁻¹. The melting point was measured by the Buchi B-545 melting point apparatus.

Synthesis of TCB

A 1-L three-necked flask was used as the reaction vessel. The middle neck was connected to a water-cooled reflux condenser equipped with a non-return gas bubbler at the top; the other neck was fitted with an argon inlet valve to create the vacuum in the system or argon flow, and the third neck of the flask was fitted with a funnel for adding the solvent or other compounds to the reaction vessel. The entire glassware was completely dried of air and moisture by simultaneously creating a high vacuum and heating with a heat gun. After cooling the glassware to room temperature, dry toluene (170 mL) and dry acetonitrile (10.5 mL, 0.2 mol) was added to the reaction flask under an argon gas atmosphere. The reaction vessel was put in a dewar flask containing a mixture of dry ice and ethanol to keep the temperature



Scheme 1

at about $-70\text{ }^{\circ}\text{C}$ to prevent the exit of volatile BCl_3 from the reaction vessel. BCl_3 solution in n-hexane (1.0 mol/L, 200 mL, 0.2 mol) was added to the flask dropwise within 2 hours while the contents of the flask were vigorously stirred. A white insoluble adduct of acetonitrile-boron trichloride began to form immediately. The reaction mixture was kept for 24 hours to form the desired adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$. The funnel was then replaced with a thermometer, and dry NH_4Cl powder (5.35 g, 0.1 mol) was added at room temperature. The mixture was stirred thoroughly with a magnetic stirrer and heated to a reflux temperature of about $86\text{ }^{\circ}\text{C}$. Hydrogen chloride gas (HCl) started to release through the bubbler violently, which was detected using pH paper. The heating was continued until no more HCl gas was detectable and ammonium chloride was dissolved. This usually requires about 10 to 12 hours. After the reaction was completed, and the mixture cooled to room temperature, the contents of the reaction flask (dark yellow liquid along with some brown precipitates) were filtered off. The solution was evaporated to dryness in vacuo. The brown crude product (ca. 90%) was purified by sublimation under vacuum (0.02 torr at $50\text{--}60\text{ }^{\circ}\text{C}$). The pure TCB was obtained as white needle-like crystals, yield: 86% (5.26 g) based on the used NH_4Cl ; m. p. $85\text{--}86\text{ }^{\circ}\text{C}$. ATR-FT-IR (cm^{-1}): 3410 (νNH), 1435 (νBN), 1035 (δNH), 806 (νBCl), 711 (δNH), 634 (δBN). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): $\delta = 5.29$ ppm (s, br, $^{14}\text{N-H}$); $^1\text{H-NMR}$ (300 MHz, Toluene- d_8 , $25\text{ }^{\circ}\text{C}$): $\delta = 4.49$ ppm (s, br, $^{14}\text{N-H}$); $^1\text{H-NMR}$ (300 MHz, Toluene- d_8 , $100\text{ }^{\circ}\text{C}$): $\delta = 4.66$ ppm (t, N-H, $^1J_{\text{N-H}} = 55$ Hz); $^{11}\text{B-NMR}$ (96 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): $\delta = 30.3$ ppm; $^{11}\text{B-NMR}$ (96 MHz, Toluene- d_8 , $25\text{ }^{\circ}\text{C}$): $\delta = 29.8$ ppm. $^{14}\text{N-NMR}$ (21 MHz Toluene- d_8 , $25\text{ }^{\circ}\text{C}$): $\delta = -271.3$ ppm.

RESULT AND DISCUSSION

Using boron trichloride (BCl_3) in gaseous form at high temperatures according to the old methods was always faced with some problems leading to low yields [23, 25]. BCl_3 is an

aggressive and poisonous gas (b. p. $12.5\text{ }^{\circ}\text{C}$) and should be liquefied with special low-temperature equipment such as a cold finger condenser and dry ice-acetone reflux condenser and kept in liquid form under extreme cold. In some studies, it was attempted to keep BCl_3 gas as liquid as possible using a coordinator compound [28].

The procedure described in the present study is a modification of the old Brown's method [8] for the facile synthesis of TCB. We used BCl_3 as a solution in n-hexane (1.0 mol/L) to achieve some significant advantages. Working with BCl_3 in liquid form is more convenient than gaseous BCl_3 , because a large amount of dangerous BCl_3 gas is released from the reaction vessel when gas is converted to liquid. In addition, it was not necessary to use special equipment for liquefying BCl_3 . Therefore, standard equipment and simple synthesis apparatus were sufficient. Acetonitrile was also used to coordinate the liquid BCl_3 , as an acetonitrile-boron trichloride adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$ to release BCl_3 slowly during the reaction (Scheme 1).

Refluxing at high temperatures, above $100\text{ }^{\circ}\text{C}$, has two negative effects on the reaction: a) increasing decomposition rate of coordinated BCl_3 in adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$ more than TCB formation rate [27], b) thermal decomposition of TCB [23], which both affect the reaction yield negatively. Hence, using BCl_3 solution in n-hexane, led to a decrease in the reflux temperature from $110\text{ }^{\circ}\text{C}$ for pure toluene to about $86\text{ }^{\circ}\text{C}$ for the mixture of toluene, acetonitrile and n-hexane. In this way, decreasing reflux temperature by about $24\text{ }^{\circ}\text{C}$ is a valuable advantage of this modified method leading to the release of coordinated BCl_3 in the adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$ gradually. Therefore, the reaction of BCl_3 with NH_4Cl powder proceeds without loss of BCl_3 , which leads to an increase in the TCB yield of about 86-90%.

Characterization and spectrometric studies of TCB

ATR-FT-IR spectrum of TCB

Because of the high sensitivity of the 2,4,6-trichloroborazine to the air and moisture, an ATR

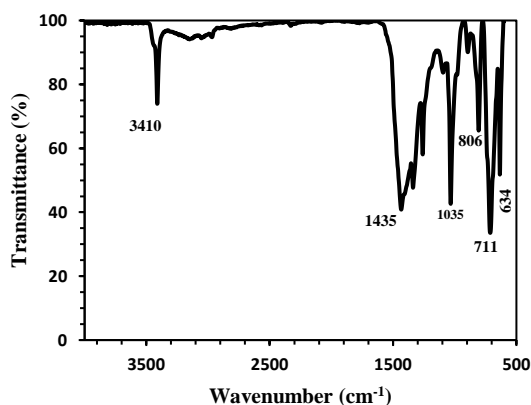


Fig. 1: ATR-FT-IR spectrum of 2,4,6-trichloroborazine (TCB).

the technique was used for infrared spectroscopy. The ATR-FT-IR spectrum of TCB (Fig. 1) indicated the presence of N-H, B-N, and B-Cl Bonds, which have already been reported [28, 30]. The stretching vibration of N-H, B-N, and B-Cl bonds was observed at 3410, 1435, and 806 cm^{-1} , respectively.

NMR-Spectra of TCB

The ^{11}B -, ^{14}N -, and ^1H -NMR spectra were performed to characterize 2,4,6-trichloroborazine (TCB). The broad signals of three equivalent ^{11}B - and ^{14}N -nuclei were observed in toluene- d_8 at $\delta = 29.8$ ppm ($h_{1/2} = 115$ Hz) and $\delta = -271.3$ ppm ($h_{1/2} = 186$ Hz), respectively (Figure 2). As it is known, nuclei with a spin I greater than $1/2$ have broad signals in NMR spectra owing to their electric quadrupole moments [31], so that the ^{11}B nucleus ($I = 3/2$) and the ^{14}N nucleus ($I = 1$) normally indicate broad signals.

The ^1H -NMR spectrum of TCB, indicates a broad peak related to the three equivalent ^{14}N -H protons in the TCB ring at room temperature, in which the expected triplet splitting owing to the $2I + 1$ orientations of a ^{14}N spin with $I = 1$, was not observed (Figure 3). As mentioned before, nuclei such as ^{14}N with the spin number $I = 1$ (i.e. I greater than $1/2$) possess an electric quadrupole moment which diminishes the spin-lattice relaxation time T_1 (i.e. the time that a nucleus needs to return to the ground state) and thereby, broadens the resonance lines [31]. The presence of the electric quadrupole moment reflects a non-spherical electric charge distribution in the nucleus which can interact with any electric field gradients of the other nucleus in its molecular environment. This interaction not only causes

a broadening of the NMR spectrum of the quadrupole nucleus but also of the resonance signal of the nucleus bonded thereto [31, 32].

It has also been reported that the electric field gradients of the electric quadrupole moment of the ^{14}N nuclei in compounds containing ^{14}N -H bonds decrease with increasing temperature. This is due to the fluctuation resulting from the molecular motions of solvent and solute [31], which leads to an increase in the spin-lattice relaxation time T_1 . In other words, ^{14}N -H spin-spin coupling constants could be observed in compounds where the quadrupole relaxation time of ^{14}N nucleus T_{qN} ($T_{qN} = T_1$) is long enough to avoid washing out the ^{14}N -H splitting in the proton spectrum [31]. Therefore, to observe the expected triplet signal of the N-H proton in the TCB molecule, the proton spectrum should be performed at elevated temperatures. We report here the ^1H -NMR spectrum of TCB at various temperatures in CDCl_3 (25, 35, 55 $^\circ\text{C}$) and in toluene- d_8 (25, 35, 55, 75, 100 $^\circ\text{C}$) for the first time (Fig. 3a).

After increasing the temperature from 25 $^\circ\text{C}$ to 35 $^\circ\text{C}$, the broad signal of N-H protons showed two shoulders, which became more distinguishable as a triplet after raising the temperature to 55 $^\circ\text{C}$ (Fig. 3a). In order to observe a better-resolved triplet, it was necessary to perform the measurements at higher temperatures so that the ^1H -NMR spectra were also performed in toluene- d_8 (Fig. 3b). First, a broad peak at $\delta = 4.49$ ppm was observed in toluene- d_8 at room temperature. The observed high field shift of about 0.8 ppm, compared to the spectrum in CDCl_3 ($\delta = 5.29$ ppm) could be attributed to the anisotropic effect of the solvent (toluene). The gradual increase in the temperature from 25 $^\circ\text{C}$ to 100 $^\circ\text{C}$ caused the broad signal to split into a clear triplet at $\delta = 4.66$ ppm with coupling constant $^1J_{(N,H)} = 55$ Hz.

In comparison to 2,4,6-trichloroborazine ($\text{B}_3\text{N}_3\text{Cl}_3\text{H}_3$), the same triplet pattern was observed for ^{14}N -H protons in the borazine ($\text{B}_3\text{N}_3\text{H}_6$) at room temperature [33]. This could be attributed to the +M-effect of the chlorine groups in the TCB, which compensates for the electron deficiency in boron atoms, and increases the electron density of the nitrogen atoms. In other words, due to the lack of chlorine groups, the electron deficiency in empty p_z -orbitals of the boron atoms in borazine could only be compensated for by nitrogen atoms' lone pairs in the form of delocalized π -electrons in the ring system ($\text{N} \rightarrow \text{B } p_z p_z (\pi)$ -dative bond) [34]. This leads to a decrease in the quadrupole moment and electric field gradients of the nitrogen atoms and

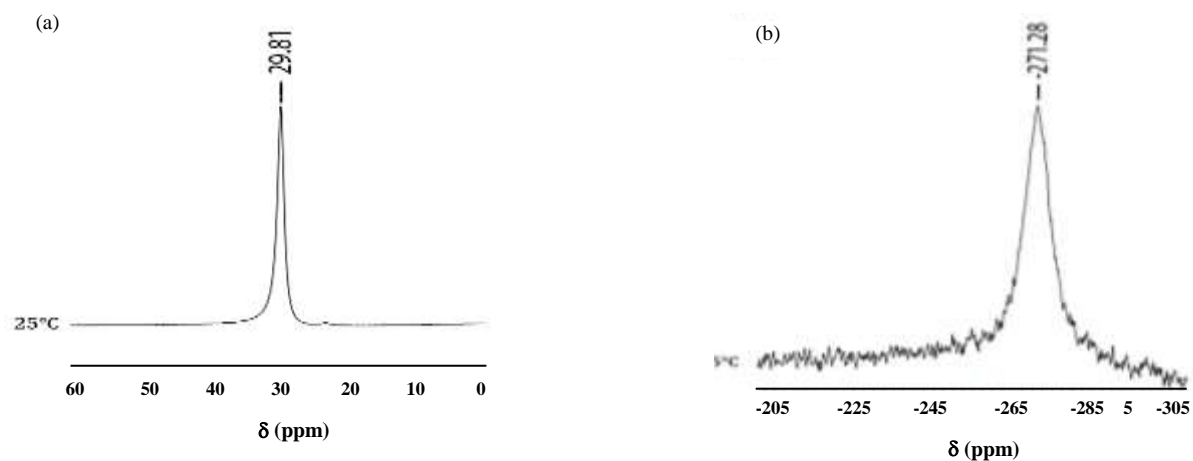


Fig. 2: The ^{11}B -NMR spectrum (a) and ^{14}N -NMR spectrum (b) of TCB in toluene- d_8 .

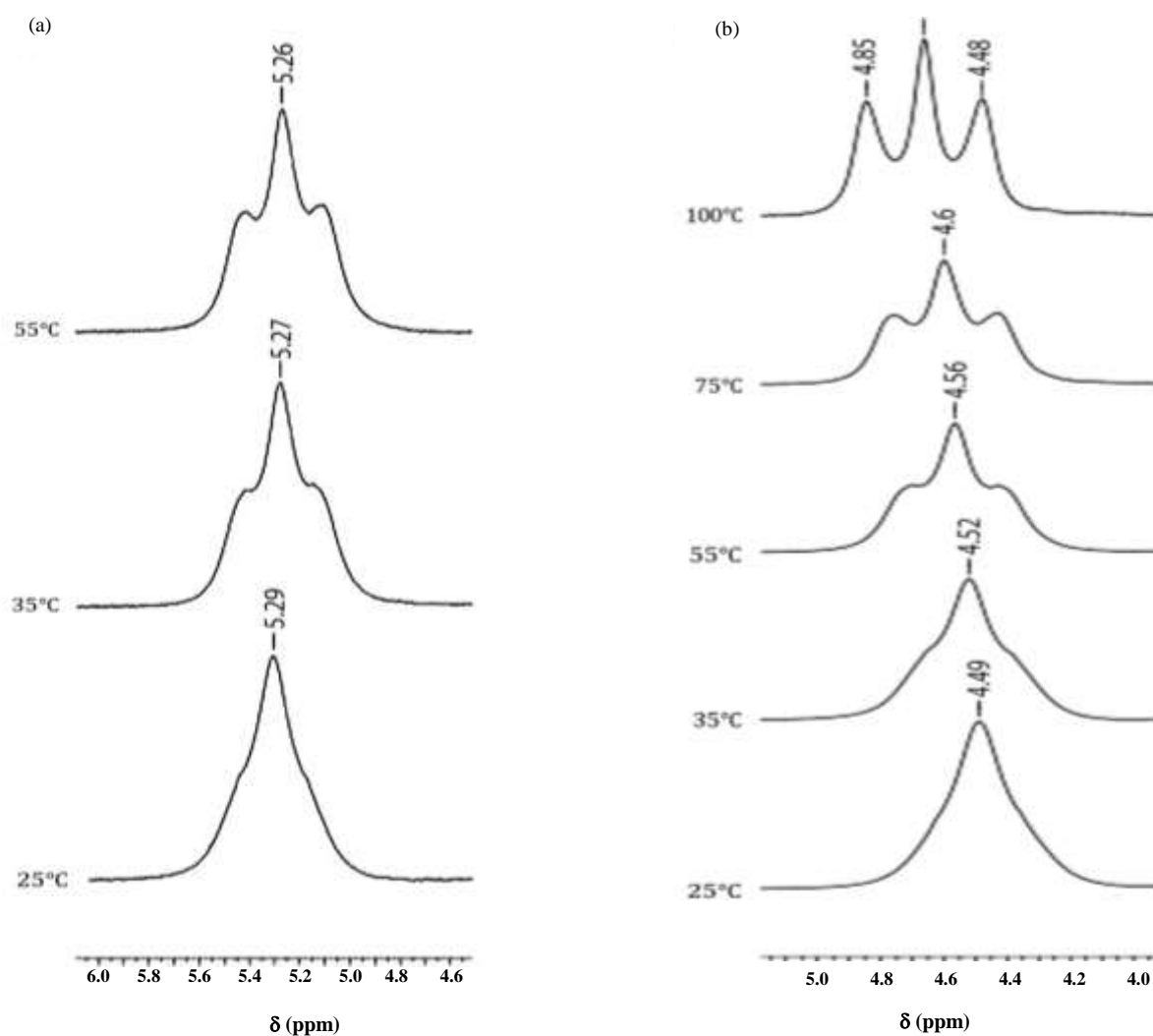


Fig. 3: The ^1H -NMR spectra of TCB at various temperatures; in CDCl_3 at 25-55 °C (a) and in toluene- d_8 at 25-100 °C (b).

to an increase in the quadrupole relaxation time of ^{14}N nuclei T_{qN} (T_1) in borazine [31]. For this reason, the expected triplet splitting of ^{14}N -H protons in borazine, can be clearly observed at room temperature and of 2,4,6-trichloroborazine at 100 °C.

CONCLUSION

2,4,6-Trichloroborazine (TCB) is the most efficient precursor for the synthesis of the widely used and strategic boron nitride compounds. TCB is a valuable and expensive compound that is needed in various industries and laboratories. Hence, any modification in the preparation method of TCB leading to the simplification of synthesis, elimination of the need for complicated equipment, decreasing reaction temperature, and energy consumption, and achieving greater purity and higher efficiency, will be appreciated.

Based on the new modification presented in our study, high purity TCB was synthesized from the reaction of BCl_3 solution in n-hexane with NH_4Cl powder using simple equipment. Utilizing BCl_3 solution in n-hexane instead of the gaseous BCl_3 as starting material avoided the loss of BCl_3 in the reaction vessel and there is no need for a cold finger condenser. The reduced reflux temperature from 132 °C for chlorobenzene to 86 °C for the mixture of toluene, acetonitrile, and n-hexane (a temperature reduction of about 46 °C) led to the slow decomposition rate of coordinated BCl_3 in the adduct complex $[\text{CH}_3\text{CN}\cdot\text{BCl}_3]$. The low reflux temperature also avoided the thermal decomposition of TCB, unwanted polymerization reactions, and the formation of undesirable products, resulting in an increased reaction yield.

For the first time, the ^1H -NMR spectra of TCB were discussed at various temperatures to evaluate the splitting of the proton resonance of the ^{14}N -H bond in the TCB ring by coupling with the ^{14}N quadrupole nucleus with the spin $I = 1$. Increasing temperature reduces the electric field gradients of the electric quadrupole moment for ^{14}N nuclei, due to the fluctuation. The fluctuation in turn results from the molecular motions of the TCB solution at elevated temperatures. The result is an increase in the relaxation time of ^{14}N nuclei T_{qN} (T_1). Therefore, the broad peak observed at room temperature was clearly split into a triplet at 100 °C due to the long T_{qN} and fast molecular motion of TCB. The ^{14}N -NMR spectrum of TCB was also shown for the first time as a broad signal at $\delta = -271.3$ ppm ($h_{1/2} = 186$ Hz).

Acknowledgments

The authors are greatly thankful to Dr. Javad Fasihi Ramandi for performing and analyzing of FT-IR spectrum by ATR technique.

Received : Nov. 28, 2021 ; Accepted : Mar. 4, 2022

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