

Theoretical Exploration on the Characterization of B-Trichloroborazine and Its Derivatives

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The B-trichloroborazine (TCB) and its derivatives with alkyl amine borazine are the effective precursor to the preparation of hexagonal BN (h-BN). On account of the specific structures of TCB and its derivatives will make some influences on the preparation reactions, in this work, by means of density functional theory, we perform a theoretical estimation of the reaction characterization of TCB and its derivatives. The results show that the order of the Wiberg bond index is $Cl > H > NHCH_3 > N(CH_3)_2$ ($1.081 > 1.002 > 0.9874 > 0.9432$). Furthermore, the gap energy of frontier orbit of TCB, $Cl_2[N(CH_3)_2]B_3N_3H_3$, $Cl[N(CH_3)_2]_2B_3N_3H_3$ and $[N(CH_3)_2]_3B_3N_3H_3$ is 784.2 KJ/mol, 666.5 KJ/mol, 695.8 KJ/mol and 674.2 KJ/mol. It is shown that the reactivity of TCB and its substituents are in the following order: $TCB < Cl[N(CH_3)_2]_2B_3N_3H_3 < [N(CH_3)_2]_3B_3N_3H_3 < Cl_2[N(CH_3)_2]B_3N_3H_3$. All the results demonstrate that the one alkyl amine derivative has the better reaction activity than TCB and the other two derivatives. Then we consider the influences on the reaction induced by the $N(CH_3)_2$ and $NHCH_3$ in the TCB derivatives. It is verified that the gap energy of the substitution reaction on $NHCH_3$ derivatives is greater than that on the $N(CH_3)_2$ derivatives, demonstrating that the derivatives of $N(CH_3)_2$ has a higher reaction activity than that of $NHCH_3$. This work should be of some significance for estimating the reaction activity and product in the preparation of h-BN.

1. Introduction

Due to the good mechanical performance, high heat conductivity and temperature resistance, stable chemical property, excellent dielectric property and other special properties, boron nitride materials have become more and more greatly application in the lubricant, thermal conductivity, hydrogen storage materials, electronic materials, aerospace and other high-tech fields, especially in the field of aerospace technology under extreme conditions of potential prospects (Paine and Narula, 1990). It can be the ablation resistance cover, electrical insulator, radar antenna window, military protection suit, anti-neutron shield and re-entry parachute, and so on (Touy et al., 2002). Therefore, it has attracted more and more attentions of scientists for materials in recent years. Among the Boron Nitride materials, the h-BN is the centre of attentions, which has the strong sp^2 covalent bond in the h-BN layer, and higher chemical and thermal stability, good lubrication, thermal conductivity, electrical insulativity and so on. From nineteen nineties the synthetic methods of h-BN got rapid development and improvement, and the research of theory and application of h-BN is also great developing. The preparation methods of h-BN material mainly include high temperature synthesis, vapor deposition, and liquid precursor method. Among them, liquid precursor method is the most important for preparing BN ceramic fibre, ceramic film, foam ceramic, ceramic coatings and ceramic matrix composites because it can control the structure and properties of h-BN material through the design of precursor molecular structure. Therefore, exploration, design and

improvement of precursor molecular structure have become a key research topic for the preparation of h-BN.

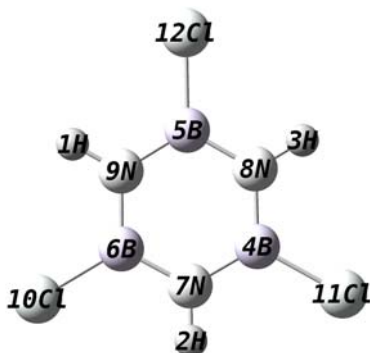


Figure 1: The optimized molecular structure and the atom labels and symbols of the TCB.

Recently, it is found that the B-Trichloroborazine (TCB, $C_1_3B_3N_3H_3$) (Figure 1) and its derivatives with alkyl amine borazine are the stable and efficient precursor to the preparation of h-BN material, and the h-BN prepared by TCB has the advantages of low sintering temperature, low content of impurities, and good processing performance. The TCB is the colorless acicular crystal at room temperature, and hydrolysis easily. Presently, the most research on the TCB are concentrated on its synthesis and molecular characteristics. Wideman (1998) has been prepared polyborazine by $NaBH_4$ and $(NH_4)_2SO_4$ in vacuum - $196\text{ }^\circ\text{C}$, and gained the spinnable polymer precursor. Miele and Cornu (2005) have been prepared the BN using TCB, and discussed the choice of reaction conditions and the yield. Furthermore, Toury (2007) has also obtained the BN, and explored the product yield by the same method. In addition, Rodriguez, Lorrette and Duperrier (2007) have prepared the TCB using boron trichloride and ammonium chloride, and prepared the amine borazine by making the reaction between TCB with methylamine and dimethylamine on the controlled conditions. The structure and properties of the amine borazine were also studied and explored. On the theoretical research, Auwärter, Suter and Greber (2004), using DFT B3LYP/6-31G (D, P) basis set, have studied and analysed the molecular structure and bonding energy of the h-BN single crystals synthesized by TCB on the Ni (111). These works show that as the h-BN precursor, the synthesis, molecular structure and modification of TCB have attracted more and more attention of scientists in the world. It is notable, the former research are mainly aims at the synthesis of TCB and its reaction with methylamine and dimethylamine, the cluster structure and properties of h-BN. It is seldom involved relationship between structure and properties of boron nitride precursor and the reaction conditions. In the present work, we theoretically studied the structure and physicochemical properties and reactivity of TCB and its derivatives by using density functional theory (DFT) and B3LYP. The results will play an important theoretical guiding significance on the control of h-BN precursor structure and selection of reaction conditions.

2. Computational Methods

All calculations of the present work are performed with Gaussian03 program package. The geometries of TCB and its derivatives with alkyl amine borazine are optimized, as well as the corresponding frequency calculations, by means of DFT with B3LYP. According to our experience (Han et al., 2011), all the atoms are used the 6-31G(d) basis set. In addition, the nature of all transition states is characterized by the imaginary frequency and verified by the intrinsic reaction coordinate (IRC) approach. All of the calculations are performed in gas phase at temperature $T = 298.15\text{ K}$ and pressure $P = 101.33\text{ kPa}$, and the energies have been modified by zero point corrections. The Wiberg bond index is accepted by the Natural Bond Orbit (NBO) calculation.

3. Results and Discussions

In this section we presented the numerical results and explored the structure and reactivity of TCB and its derivatives. The optimized molecular structure and the atom labels and symbols of the TCB and its

derivatives substituted of one NHCH_3 and $\text{N}(\text{CH}_3)_2$ are shown in Figure 1 and Figure 2. It can be found that the structure of the TCB and its alkyl amine derivatives are mainly composed of a plane six ring, causing many special physical and chemical properties of them.

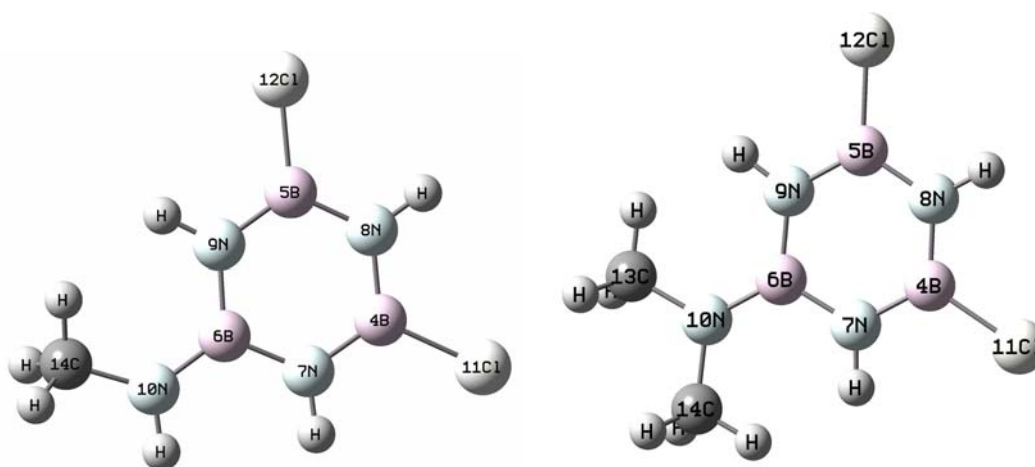


Figure 2: The optimized molecular structure and the atom labels and symbols of the one NHCH_3 and $\text{N}(\text{CH}_3)_2$ substituted TCB derivatives.

3.1 Wiberg bond index

In order to explore the reaction activity of TCB and its alkyl amine derivatives, we performed the NBO analysis and calculation by DFT. The Wiberg bond index of TCB, dimethylamine derivatives and methylamine derivatives are listed in Table 1 and Table 2.

Table 1: The Wiberg bond index of TCB and dimethylamine derivatives

bonds	TCB	$\text{Cl}_2[\text{N}(\text{CH}_3)_2]\text{B}_3\text{N}_3\text{H}_3$	$\text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$	$[\text{N}(\text{CH}_3)_2]_3\text{B}_3\text{N}_3\text{H}_3$
B4-Cl11/N7	1.112	1.080	0.9705	0.9432
N7-H2	0.7697	0.7741	0.7887	0.8038
B5-Cl12	1.112	1.080	1.052	0.9434
N8-H3	0.7697	0.7849	0.7887	0.8037
B6-Cl10/N10	1.112	0.9971	0.9706	0.9435
N9-H1	0.7697	0.7849	0.7996	0.8037

Table 2: The Wiberg bond index of TCB and methylamine derivatives

bonds	TCB	$\text{Cl}_2(\text{NHCH}_3)\text{B}_3\text{N}_3\text{H}_3$	$\text{Cl}(\text{NHCH}_3)_2\text{B}_3\text{N}_3\text{H}_3$	$(\text{NHCH}_3)_3\text{B}_3\text{N}_3\text{H}_3$
B4-Cl11/N7	1.112	1.041	1.013	0.9904
N7-H2	0.7697	0.7882	0.7927	0.8085
B5-Cl12	1.112	1.080	1.052	0.9874
N8-H3	0.7697	0.7850	0.8041	0.8122
B6-Cl10/N10	1.112	1.080	1.015	0.9891
N9-H1	0.7697	0.7744	0.7894	0.8048

From Table 1, we can find that the Wiberg bond index of B-Cl/N on TCB, $\text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$, $[\text{N}(\text{CH}_3)_2]_3\text{B}_3\text{N}_3\text{H}_3$, $\text{Cl}_2[\text{N}(\text{CH}_3)_2]\text{B}_3\text{N}_3\text{H}_3$ are 1.112, 1.080, 0.9705 and 0.9432 respectively, demonstrating that the stability of them is following: $\text{TCB} > \text{Cl}_2[\text{N}(\text{CH}_3)_2]\text{B}_3\text{N}_3\text{H}_3 > \text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3 > [\text{N}(\text{CH}_3)_2]_3\text{B}_3\text{N}_3\text{H}_3$. This order also can be found from methylamine derivatives on Table 2. Contrasting Table 1 with Table 2, it can be found that the bond index of B-Cl, B-H, B-NHCH₃, B-N(CH₃)₂ and N-H are 1.112, 1.002, 0.9874, 0.9432 and 0.7697. It is shown that B-Cl bond is the most stable than the other bonds, and the stability of them is $\text{B-Cl} > \text{B-H} > \text{B-NHCH}_3 > \text{B-N}(\text{CH}_3)_2 > \text{N-H}$, in accordance with the literature

(Coursen and Hoard, 1952). It also can be demonstrated that the reaction activity of $N(CH_3)_2$ derivatives is bigger than that of $NHCH_3$.

3.2 The gap energy of frontier orbit

Furthermore, we consider the variation of the gap energy of frontier orbit ($\Delta E_{LUMO-HOMO}$) of TCB and its derivatives. The $\Delta E_{LUMO-HOMO}$ of TCB, dimethylamine and methylamine derivatives are listed in Table 3 and Table 4. Obviously, it can be found that the $\Delta E_{LUMO-HOMO}$ of one dimethylamine (or methylamine) substituted TCB is the lower than that of the other derivatives, the $\Delta E_{LUMO-HOMO}$ order of them is TCB (784.2 KJ/mol) > $Cl_2[N(CH_3)_2]_2B_3N_3H_3$ (695.8 KJ/mol) > $[N(CH_3)_2]_3B_3N_3H_3$ (674.2 KJ/mol) > $Cl_2[N(CH_3)_2]B_3N_3H_3$ (666.5 KJ/mol). It is demonstrated that the reactivity of TCB and its dimethylamine derivatives is $TCB < Cl_2[N(CH_3)_2]_2B_3N_3H_3 < [N(CH_3)_2]_3B_3N_3H_3 < Cl_2[N(CH_3)_2]B_3N_3H_3$, and one amine substituted TCB has the better reaction activity than TCB and the other two derivatives. These results are also able to be found from the methylamine derivatives, as well as the one methylamine substituted TCB of the better reaction activity than the other two derivatives (as shown in Table 4).

In addition, contrasting Table 3 with Table 4, it can be found that the $\Delta E_{LUMO-HOMO}$ of dimethylamine substitutes are always lower than that of the same substituted methylamine derivatives, shown that the derivatives of $N(CH_3)_2$ have a higher reaction activity than that of $NHCH_3$.

Table 3: The $\Delta E_{LUMO-HOMO}$ of TCB and dimethylamine derivatives

bonds	TCB	$Cl_2[N(CH_3)_2]_2B_3N_3H_3$	$Cl[N(CH_3)_2]_2B_3N_3H_3$	$[N(CH_3)_2]_3B_3N_3H_3$
$\Delta E_{LUMO-HOMO}$ (KJ/mol)	784.2	666.5	695.8	674.2

Table 4: The $\Delta E_{LUMO-HOMO}$ of TCB and methylamine derivatives

bonds	TCB	$Cl_2(NHCH_3)B_3N_3H_3$	$Cl(NHCH_3)_2B_3N_3H_3$	$(NHCH_3)_3B_3N_3H_3$
$\Delta E_{LUMO-HOMO}$ (KJ/mol)	784.2	691.1	724.4	723.3

3.3 The gap energy of the reaction

In order to study the reactivity of TCB and its derivatives we modeled all the reactions occurred from TCB to three alkyl amine derivatives, and the reaction process is shown in Figure 4. The corresponding reaction activation energies and the gap energy (defined as $\Delta E = E_p - E_R$ with E_p and E_R being the energy of the product and the reactants) are shown in Figure 5. By comparing the reaction activation energies Δ^*E_1 , Δ^*E_2 and Δ^*E_3 corresponding to the first, second and three steps in substituted reaction, we can find Δ^*E_1 is always larger than Δ^*E_2 and Δ^*E_3 , clearly demonstrating that the first step is the rate determining one. In addition, it also can be found that Δ^*E_2 is always lower than Δ^*E_1 and Δ^*E_3 , demonstrated that the one alkyl amine derivative has the best reactivity than TCB and the other two derivatives.

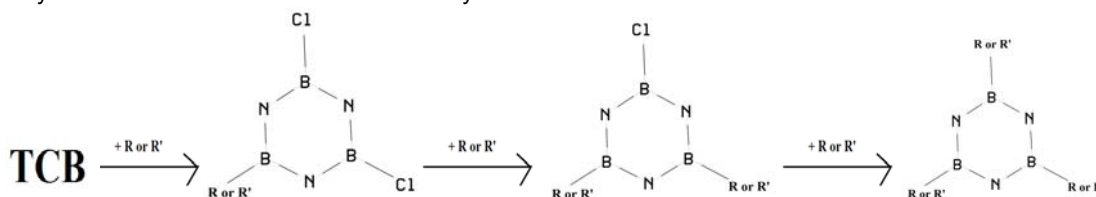


Figure 4: The reaction process from TCB to its derivatives of $R=NHCH_3$ and $R'=N(CH_3)_2$.

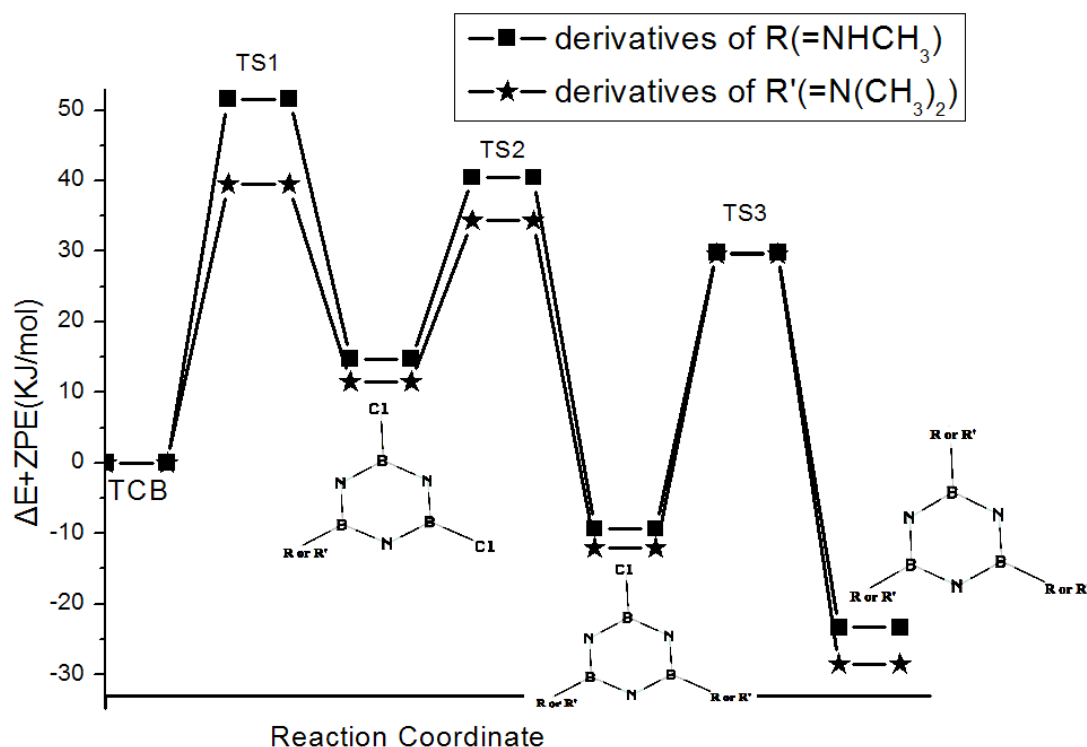


Figure 5: The gap energy of the reaction from TCB to its derivatives of NHCH_3 and $\text{N}(\text{CH}_3)_2$.

Furthermore, we can find that the activation energy Δ^*E_1 of the first step will become large from 39.46 KJ/mol to 51.56 KJ/mol when substituent $\text{N}(\text{CH}_3)_2$ is changed to NHCH_3 , in the same way, the activation energy of the second and three step changes from 34.31 KJ/mol to 40.47 KJ/mol and from 29.58 KJ/mol to 29.80 KJ/mol, which seemingly indicates that the derivatives of $\text{N}(\text{CH}_3)_2$ has a high reactivity than that of NHCH_3 . This result can also be found from the $\Delta E_{\text{LUMO-HOMO}}$ variation of the TCB and its derivatives in Table 3 and Table 4. From Figure 2, it can also be found that the energies of the products will decrease with substituent NHCH_3 changing to $\text{N}(\text{CH}_3)_2$, indicating that the products become more stable in substituent $\text{N}(\text{CH}_3)_2$, consistent with a great many experimental studies.

4. Conclusion

In conclusion, we have studied the reactivity and stability of TCB and its derivatives by comparing and analyzing the molecular structure, the gap energy, and the Wiberg bonds. It is shown that the one alkyl amine derivative has the best reaction activity than TCB and the other two derivatives, and the derivatives of $\text{N}(\text{CH}_3)_2$ has a more stability than that of NHCH_3 . This is beneficial to control the shape and appearance of the BN on the production process. The results of this work can be seen as a parameter to estimating the reaction activity and product in the preparation of h-BN, reduce the energy consumption and reaction time in the current production methods.

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References

Auwärter W., Suter H. U., Sachdev H., Greber T., Synthesis of one monolayer of hexagonal boron nitride on Ni(111) from B-Trichloroborazine (Cl_3BNH)₃, Chem Mater., 2004, 16, 343-345.

- Cornu D., Bernard S., Duperrier S., Toury B., Miele P., Alkylaminoborazine-based precursors for the preparation of boron nitride fibers by the polymer-derived ceramics (PDCs) route, *J. Eur. Ceram. Soc.*, 2005, 25, 111-121.
- Coursen D. L., and Hoard J. L., 1952, The Structure of B-Trichloroborazole, *J. Am. Chem. Soc.*, 74(7), 1742-1750.
- Duperrier S., Bernard S., Calin A., Sigala C., Chiriac R., Miele P., Balan C., Design of a Series of Pre-ceramic B-Tri(methylamino)borazine-Based Polymers as Fiber Precursors: Shear Rheology Investigations, *Macromolecules*, 2007, 40, 1028-1034.
- Han Q. Z., Zhang H. Z., Zhao Y. H., Wen H., 2011, Theoretically Study on the Reaction Complexing Olefins with Nickel Dithiolene, *Chemical Engineering Transactions*, 25, 171-176, DOI: 10.3303/CET1125029
- Xu J.B., Zhang S. F., Wu H., Zhao Y.H., Wen H., 2011, Mesoscopic Simulation of Aggregate Structure and Stability of Heavy Crude Oil by Gpu Accelerated Dpd , *Chemical Engineering Transactions*, 24, 1531-1536, DOI: 10.3303/CET1124256
- Lorrette C., Weisbecker P., Jacques S., Deposition and characterization of hex-BN coating on carbon fibres tris(dimethylamino)boron precursor, *J Eur. Ceram. Soc.*, 2007, 27, 2737-2743.
- Miele P., Bernard S., Cornu D., Recent developments in polymer-derived ceramic fibers (PDCFs): Preparation, properties and applications, *Soft Mater*, 2007, 4, 249–286.
- Paine R. T., Narula C. K., Synthetic routes to boron nitride, *Chem. Rev.*, 1990, 90(1), 73—91.
- Rodriguez M. A., Borek T. T., 1,3-Dichloro-5-(dimethylamino)borazine, *Acta. Cryst.*, 2007, E63, 2638
- Toury B., Miele P., Cornu D., Boron nitride fibers prepared from symmetric and asymmetric alkylaminoborazines, *Adv. Funct. Mater*, 2002, 12(3), 228–234.
- Toury B., Cornu D., Chassagneux F., Miele P., Complete characterisation of BN fibres obtained from a new polyborylborazine, *J Euro. Cera. Soc.*, 2005, 25, 137-141.
- Wideman T., Remsen E. E., Cortez E., Amine-modified polyborazylenes: Second generation precursors to boron nitride, *Chem Mater*, 1998, 10(1), 412–421.