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Theoretical study of unusual Bis(amino)(2,4,6-*tri*-*t*-butylphenyl)borane $B(NH_2)_2NHAr)$

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Abstract

Theoretical study of unusual Bis(amino)(2,4,6-*tri*-*t*-butylphenyl)borane ($B(NH_2)_2NHAr$) which is formed from BCl_2NHAr and an excess of liquid ammonia has been carried out. This compound has trigonal planar boron atom with two B─NH_2 bonds has a no significant change, B─N(9) and B─N(10) are 1.471 Å, 1.450 Å respectively and each longer than the B─NHAr (B─ N(7), which is equal to 1.480 Å, so the three B─N bonds are non-equivalent. The most interesting part (BN_3) moiety in this compound is planar and formed an angle with the aromatic ring plane. The bond lengths, bond angles, dihedral angles and close contact of atoms were showed variable results and the conjugation was also affect the results. Internal coordinate was also calculated. Molecular mechanics MM2 properties were calculated due to high Van der Waals (VDW) interactions, some terms were not computed. MM2 minimization were calculated, the results indicated that the minimization was done successfully.

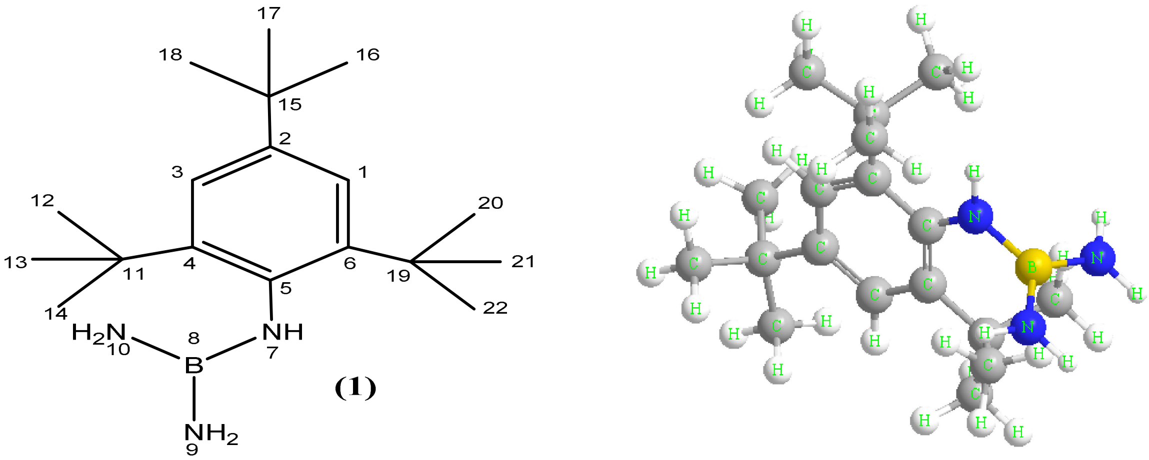
Key words: Internal coordinate, molecular mechanics, unusual boron amide

Introduction

The unusual *Bis*(amino)(2,4,6-*tri*-*t*-butylphenyl)borane ($B(NH_2)_2NHAr$) is the first stable borane compound to contain a pair of germinal NH_2 group [1]. This compound contain bulky aryl group (2,4,6-*tri*-*t*-butyl phenyl). A survey on the chemistry of such borane containing single NH_2 has been discussed [2]. A studies concerning structural and bonding on new families of functional boron compounds practically clusters [3]. G. Jayasree reviewed well-recognized analogies between boron and carbon and describe the connection that have been overlooked [4]. Another study developed a variety of the boron electron counting rules to predict a new class of polyhedral cage [5]. A theoretical study on cyclo-*tetra* boranes has been studied [6]. Internal co-ordinates are an attractive alternative to the Cartesian coordinates of each atom when particular degrees of freedom are not of interest [7]. Internal coordinates such as bond lengths, bond angles, and torsion angles (BAT) are natural coordinates for describing a bonded molecular system [8]. One of the major advantages of molecular mechanics compared to other computational techniques is the relative ease with which structures can be optimized via minimization of the corresponding potential energy functions [9].

Result and dissection

Theoretical studies carried on unusual Bis(amino)(2,4,6-*tri*-*t*-butylphenyl)borane ($B(NH_2)_2NHAr$) (Figure 1). Analysis of the compound showed that the exact mass of $C_{18}H_{34}BN_3$ was equal to 303.2846 and the abundance was 65%.



(1)

Figure 1: The Bis(amino)(2,4,6-*tri*-*t*-butylphenyl)borane ($B(NH_2)_2NHAr$)

The elemental analysis also theoretically calculated by chem. draw which shows: C, 69.89; H, 13.03; B, 3.49 and N, 13.58. From the bond angle presented in (table 1), the sum of the angles around the B atom is 360^o so the boron atom is planar with SP^2-hybridisation. The particular bond lengths of $B(NH_2)_2NHAr$ are provided in table 1 below in order to study the internal coordinate, they are in accordance with already reported structures in (figure 1). The carbon — carbon bond length of the bulky group that attached to the ring are single bonds and it has sp^3 hybridization from the bond angles which are equal to 109°. The B—N(7)Å bond length (1.480)Å is in conflict with that found by studying the compound by X-Ray crystallography (1.410)Å and that may be related to state of the crystal and the refinement**.** However, the three B—N bond lengths are significantly longer in comparison with the X-ray diffraction studies[1]. Within the molecule the three B-N bond distances are surprisingly different the bonds B—N (7), B— N (9) and B— N (10) are 1.480 Å, 1.471 Å and 1.450 Å respectively. These bonds significantly longer than the B-N bond length that found in the simplest BN compounds (1.403 Å) obtained from microwave studies and that found in the four coordinate analogue which found in B $(NMe_2)_3$ (1.431 Å) in the vapour phase and (1.439 Å) in the crystal at low temperature. The B—N (9) bond length (1.471 Å) is significantly longer than the B—N (10) suggesting a reduced in (p-p) π interaction with B atom and this may be connected with the fact that the chain of atoms C(5) —N(7) —B—N(9) curves round towards the underside of the aromatic ring. This means that one of the hydrogen atoms would be close to the ring and co-planar with BN_3. The dihedral angles were also calculated accordance with already reported structure in figure 1 in order to study the internal coordinate of $B(NH_2)_2NHAr$.

Table 1: The internal coordinates for (B $(NH_2)_2$NHAr)

No	Atom	Bond Atom	Bond Length (Å)	Angle Atom	Angle (°)	2nd Angle Atom	2nd Angle (°)	2nd Angle Type
1	C(1)							
2	C(2)	C(1)	1.395					
3	C(3)	C(2)	1.395	C(1)	119.997			
4	C(15)	C(2)	1.497	C(1)	120.002	C(3)	120.002	Pro-R
5	C(4)	C(3)	1.395	C(2)	120	C(1)	-0.006	Dihedral
6	H(24)	C(3)	1.1	C(2)	120	C(4)	120	Pro-S
7	C(5)	C(4)	1.395	C(3)	120.003	C(2)	0.001	Dihedral
8	C(11)	C(4)	1.497	C(3)	119.998	C(5)	119.998	Pro-R
9	C(6)	C(1)	1.395	C(2)	120.003	C(3)	0.006	Dihedral
10	N(7)	C(5)	1.266	C(4)	120.001	C(6)	120.001	Pro-S
11	C(19)	C(6)	1.497	C(1)	120	C(5)	120	Pro-S
12	H(23)	C(1)	1.1	C(2)	119.998	C(6)	119.999	Pro-S
13	B	N(7)	1.480	C(5)	120	C(4)	-180	Dihedral
14	H(25)	N(7)	1.050	C(5)	120	B	120	Pro-S
15	N(9)	B	1.471	N(7)	120	C(5)	-90	Dihedral
16	N(10)	B	1.450	N(7)	120	N(9)	120	Pro-S
17	C(12)	C(11)	1.523	C(4)	109.5	C(3)	0	Dihedral
18	C(13)	C(11)	1.523	C(4)	109.442	C(12)	109.442	Pro-S
19	C(14)	C(11)	1.523	C(4)	109.462	C(12)	109.462	Pro-R
20	C(16)	C(15)	1.523	C(2)	109.5	C(1)	0	Dihedral
21	C(17)	C(15)	1.523	C(2)	109.442	C(16)	109.442	Pro-S
22	C(18)	C(15)	1.523	C(2)	109.462	C(16)	109.462	Pro-R
23	C(20)	C(19)	1.523	C(6)	109.5	C(1)	0	Dihedral
24	C(21)	C(19)	1.523	C(6)	109.442	C(20)	109.442	Pro-S
25	C(22)	C(19)	1.523	C(6)	109.462	C(20)	109.462	Pro-R
26	H(26)	N(9)	1.02	B	120	N(7)	-180	Dihedral
27	H(27)	N(9)	1.02	B	120	H(26)	120	Pro-S
28	H(28)	N(10)	1.02	B	120	N(7)	-180	Dihedral
29	H(29)	N(10)	1.02	B	119.999	H(28)	120	Pro-S
30	H(30)	C(12)	1.113	C(11)	109.5	C(4)	-180	Dihedral
31	H(31)	C(12)	1.113	C(11)	109.442	H(30)	109.442	Pro-S
32	H(32)	C(12)	1.113	C(11)	109.462	H(30)	109.462	Pro-R
33	H(33)	C(13)	1.113	C(11)	109.5	C(4)	180	Dihedral
34	H(34)	C(13)	1.113	C(11)	109.442	H(33)	109.442	Pro-R
35	H(35)	C(13)	1.113	C(11)	109.462	H(33)	109.462	Pro-S
36	H(36)	C(14)	1.113	C(11)	109.5	C(4)	0	Dihedral
37	H(37)	C(14)	1.113	C(11)	109.442	H(36)	109.441	Pro-S
38	H(38)	C(14)	1.113	C(11)	109.462	H(36)	109.462	Pro-R
39	H(39)	C(16)	1.113	C(15)	109.5	C(2)	-180	Dihedral
40	H(40)	C(16)	1.113	C(15)	109.442	H(39)	109.442	Pro-S
41	H(41)	C(16)	1.113	C(15)	109.462	H(39)	109.462	Pro-R
42	H(42)	C(17)	1.113	C(15)	109.5	C(2)	-180	Dihedral
43	H(43)	C(17)	1.113	C(15)	109.442	H(42)	109.442	Pro-R
44	H(44)	C(17)	1.113	C(15)	109.461	H(42)	109.462	Pro-S
45	H(45)	C(18)	1.113	C(15)	109.5	C(2)	0	Dihedral
46	H(46)	C(18)	1.113	C(15)	109.442	H(45)	109.441	Pro-S
47	H(47)	C(18)	1.113	C(15)	109.462	H(45)	109.462	Pro-R
48	H(48)	C(20)	1.113	C(19)	109.5	C(6)	180	Dihedral
49	H(49)	C(20)	1.113	C(19)	109.442	H(48)	109.442	Pro-S
50	H(50)	C(20)	1.113	C(19)	109.462	H(48)	109.462	Pro-R
51	H(51)	C(21)	1.113	C(19)	109.5	C(6)	180	Dihedral
52	H(52)	C(21)	1.113	C(19)	109.442	H(51)	109.442	Pro-R

Internal coordinates of B $(NH_2)_2NHAr$ were displayed that the atoms configuration were in R and S and the angle type was dihedral in most of atoms. Thus the dihedral angles were also calculated accordance with already reported structure in figure 1 in order to study the internal coordinate of, (Table 2).

Table 2: Selected dihedral angles for in (B $(NH_2)_2NHAr$)

No	Atoms	Dihedral Angle°
1	C(5)-N(7)-B—N(9)	-90
2	C(5)-N(7)-B—N(10)	90
3	C(1)-C(6)-C(19)-C(20)	0
4	C(1)-C(6)-C(19)-C(21)	119.964
5	C(1)-C(6)-C(19)-C(22)	-120
6	C(5)-C(6)-C(19)-C(20)	180
7	C(5)-C(6)-C(19)-C(21)	-60.036
8	C(5)-C(6)-C(19)-C(22)	60
9	C(4)-C(5)-C(6)-C(1)	-0.003
10	C(4)-C(5)-C(6)-C(19)	179.997
11	N(7)-C(5)-C(6)-C(1)	179.997
12	N(7)-C(5)-C(6)-C(19)	-0.003
13	C(4)-C(5)-N(7)-B	-180
14	C(6)-C(5)-N(7)-B	0
15	C(3)-C(4)-C(5)-N(7)	-179.997
16	C(3)-C(4)-C(5)-C(6)	0.003
17	C(11)-C(4)-C(5)-N(7)	0.003
18	C(11)-C(4)-C(5)-C(6)	-179.997
19	C(3)-C(4)-C(11)-C(12)	0
20	C(3)-C(4)-C(11)-C(13)	119.963
21	C(3)-C(4)-C(11)-C(14)	-120
22	C(5)-C(4)-C(11)-C(12)	180
23	C(5)-C(4)-C(11)-C(13)	-60.036
24	C(5)-C(4)-C(11)-C(14)	60
25	C(2)-C(3)-C(4)-C(11)	-179.999
26	C(2)-C(3)-C(4)-C(5)	0.001
27	C(1)-C(2)-C(3)-C(4)	-0.006
28	C(15)-C(2)-C(3)-C(4)	179.994
29	C(1)-C(2)-C(15)-C(16)	0
30	C(1)-C(2)-C(15)-C(17)	119.964
31	C(1)-C(2)-C(15)-C(18)	-120
32	C(3)-C(2)-C(15)-C(16)	180
33	C(3)-C(2)-C(15)-C(17)	-60.036
34	C(3)-C(2)-C(15)-C(18)	60
35	C(2)-C(1)-C(6)-C(5)	-0.001
36	C(2)-C(1)-C(6)-C(19)	179.999
37	C(6)-C(1)-C(2)-C(15)	-179.994
38	C(6)-C(1)-C(2)-C(3)	0.006

Table (2) demonstrated that the dihedral angle of C(5)-N(7)-B-N(9) and C(5)-N(7)-B-N(10) were equal to -90 and 90 respectively and this indicate the earlier results, but the N(7)-C(5)-C(6)-C(1) and N(7)-C(5)-C(6)-C(19) were equal to 179.997 and -0.003 respectively and this correlated to different bonding in between the atoms corresponding to N-C-C=C and N-C-C-C respectively. The dihedral angle in C(6)-C(5)-N(7)-B and C(4)-C(5)-N(7)-B were equal to 0 and -180 corresponding to C-C-N-B and C=C-N-B respectively. All dihedral angles were calculated with respect the structure presented in figure 1. Further, the close contact of selected atoms in B $(NH_2)_2NHAr$ were studied as seen in table 3 below.

Table 3: Close contact of selected atoms in ($B(NH_2)_2NHAr$)

No	Atoms	Close Contact Atoms
1	N(9)-C(22)	1.597
2	B─C(22)	2.096
3	N(10)-C(21)	1.598
4	B─C(21)	2.096
5	C(1)-C(20)	2.712
6	C(1)-C(16)	2.712
7	C(3)-C(12)	2.712
8	C(19)-N(10)	2.73
9	C(19)-N(9)	2.73
10	C(19)-B	2.305
11	C(6) ─B	2.713
12	N(7)-C(19)	2.784
13	C(11)-N(7)	2.783
14	C(3)-C(6)	2.79
15	C(2)-C(5)	2.79
16	C(1)-C(4)	2.79

Table (3) presented the close contact of selected atoms in compound (1), for example B─ C(22) and B─C(21) were gave 2.096 in each corresponding to B-N-C-C-C-C net of bonding, but the C(3)-C(6), C(2)-C(5) and C(1)-C(4) were gave 2.79 in each related to the conjugation effect in aromatic ring and this can affect the results while N(9)-C(22) and N(10)-C(21) are very close 1.597 and that leave the hydrogen atom on N(7) close to the other t-butyl .Further, the internal coordinate for ($B(NH_2)_2NHAr$) was calculated as seen in table (1) above. The table displayed the effect of the unusual boron amide B $(NH_2)_2NHAr$ in the internal coordinate of the compound. It was also indicated the difference in the bonds length of B─N (7), B─N (9) and B─N (10) which equal to 1.480 Å, 1.471 Å and 1.450 Å respectively. MM2 Properties were also calculated, (Pi System: 1 2 3 4 6 5 7), shows (Stretch: 12.3627, Bend: 217.4488, Stretch-Bend: -0.1463, Torsion: 2.4668, Non-1,4 VDW 1236.3710, 1,4 VDW: 23.9552 and Total Energy: 1492.4582 kcal/mol), Due to high VDW interactions, due to MM2 minimization shows (pi system: 1 2 3 4 6 5 7) (Stretch: 5.0573, Bend: 9.2631, Stretch-Bend: 0.4439, Torsion: -4.4351, Non-1,4 VDW: 0.4910, 1,4 VDW: 14.3692, Dipole/Dipole: -0.5005, Total Energy: 24.6888 kcal/mol), the results indicated that the minimization was done successfully

Experimental section

The compound $B(NH_2)_2NHAr$ was prepared from BCl_2NHAr and an excess of liquid ammonia as in equation 1 below$^{(1)}$.

$$\mathbf{BCl_2NHAr + NH_3 \xrightarrow[25^oC]{C_6H_{14}} B(NH_2)_2NHAr} \text{ ------ } \mathbf{(1)}$$

Theoretical studies were done using molecular mechanics program to study the structure details, physical properties of molecules and to calculates the energy of a molecule then adjusts the energy through changes in the bond lengths and angles in which to obtain the minimum energy structure.The semi-empirical methods on hyper chem. Program version 7.5 was also used to calculate some bond lengths and bond angles in which the result nearly the same especially in the BN3 moiety.

Summary

The area of this work to study the unusual Boran amide which has three B-N bond distances are surprisingly different and the most interesting part (BN_3) moiety in this compound is planar and formed an angle with the aromatic ring plane. Molecular mechanics is to study the detailed structure and physical properties of this molecule. Molecular mechanics calculates the energy of a molecule and then adjusts the energy through changes in the bond lengths and angles to obtain the minimum energy structure. Internal coordinate also have some advantages for suggesting a new derivatives.

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