



# WEIRD CHEMIST

## P-Block Elements — Solutions

### Back Bonding

DPP – 01

Topic: Back Bonding

Questions: 15 Questions

Exam: JEE / NEET

### ▶ TYPE 1 : Back Bonding in $\text{BF}_3$ — Bond Properties & Structure

#### Key Concepts — Back Bonding in $\text{BF}_3$

- B in  $\text{BF}_3$  is  $sp^2$ -hybridised with one **empty**  $p$  orbital perpendicular to the molecular plane
- F has **filled**  $2p$  lone pairs that overlap sideways with B's empty  $2p$  orbital  $\Rightarrow p\pi-p\pi$  back bonding
- Result: B–F gets **partial double bond** character; bond order  $> 1$ ; bond shorter and stronger than expected
- Three equivalent resonance structures  $\Rightarrow$  bond is **delocalised**
- When a Lewis base donates to B (e.g.  $\text{Me}_3\text{N}$ ), B's empty orbital is filled  $\Rightarrow$  back bonding **stops**  $\Rightarrow$  bond length **increases**

#### Q1. In $\text{BF}_3$ :

##### Explanation

B in  $\text{BF}_3$  is  $sp^2$ -hybridised, leaving one **empty**  $2p$  orbital on B perpendicular to the molecular plane. Each F has filled  $2p$  lone pairs in the same plane as this empty orbital. F's lone pair overlaps sideways with B's empty  $p$  orbital ( $p\pi-p\pi$  back bonding). This gives the B–F bond **partial double bond character**. Since all three F atoms do this equally, three equivalent resonance structures exist  $\Rightarrow$  the bonds are **delocalised**. Option (1) correctly captures both facts.

##### Approach

Think of B's empty  $p$  orbital as an empty cup. Each F has a filled cup (lone pair) held sideways next to it. Some electron density "spills" from F into B — that's back bonding. Since all three F atoms spill equally, the extra bond character is smeared (delocalised) across all three B–F bonds.

##### Answer

(1) B–F bond has some double bond character and this bond is delocalised.

#### Q2. Which of the following statements is incorrect about the B–F bond in $\text{BF}_3$ ?

### Explanation

Statements (1), (2), (3) are all correct facts about  $\text{BF}_3$ .

Statement (4) is **incorrect**: it says  $p\pi-d\pi$  interaction. B is a **2nd-period** element — it has **no  $d$  orbitals** available for bonding. The back bonding in  $\text{BF}_3$  is strictly  $p\pi-p\pi$ : F's filled  $2p$  donates into B's empty  $2p$ . A  $p\pi-d\pi$  interaction would require B to have  $d$  orbitals, which only happens from the 3rd period onwards (e.g. Si, P, S).

### Approach

Quick rule:  $d$  orbitals are only available from Period 3 onwards. B is in Period 2  $\Rightarrow$  only  $s$  and  $p$  orbitals  $\Rightarrow$  any  $d$ -orbital mention for B is automatically wrong.

### Answer

(4) The  $p\pi-d\pi$  explanation is incorrect; it is a  $p\pi-p\pi$  interaction.

**Q3. In  $\text{BF}_3$ , B–F bond length = 1.30 Å. When  $\text{BF}_3$  reacts with  $\text{Me}_3\text{N}$  to form  $[\text{Me}_3\text{N} \rightarrow \text{BF}_3]$ , the B–F bond length in the adduct is:**

### Explanation

In free  $\text{BF}_3$ : B's  $p$  orbital is empty  $\Rightarrow$  back bonding from F is strong  $\Rightarrow$  B–F has partial double bond character  $\Rightarrow$  bond length = 1.30 Å (shorter than a pure single bond).

In the adduct  $[\text{Me}_3\text{N} \rightarrow \text{BF}_3]$ :  $\text{Me}_3\text{N}$ 's lone pair fills B's empty  $p$  orbital. B changes  $sp^2 \rightarrow sp^3$ . Now B has **no empty orbital**  $\Rightarrow$  back bonding from F **completely stops**  $\Rightarrow$  B–F becomes a pure single bond  $\Rightarrow$  bond length **increases** beyond 1.30 Å.

### Approach

The empty cup (B's  $p$  orbital) is now filled by  $\text{Me}_3\text{N}$ . F can no longer donate  $\Rightarrow$  bond order drops from  $\sim 1.5$  to 1.0  $\Rightarrow$  bond gets longer.

### Answer

(1) Greater than 1.30 Å.

**Q4. Which structure correctly represents the boron trifluoride molecule?**

### Explanation

$\text{BF}_3$  has **three** resonance structures. In each, one B–F bond is shown as a **double bond** with no formal charges on B (B is neutral, the double-bond F is also neutral). The other two F atoms carry single bonds. This is Structure (1): three equivalent resonance contributors where each F takes a turn forming the double bond with B.

Structure (2) shows only two resonance structures  $\Rightarrow$  incorrect (all three F atoms must be equivalent).

Structures (3) and (4) place formal charges on  $B^+$  and  $F^-$ , implying an ionic resonance that is not the primary description.

### Approach

In the correct resonance set for  $BF_3$ : 3 structures, no formal charges, one double bond each. If you see charges in the dominant structures, it is wrong.

### Answer

(1) Structure 1.

## ▶ TYPE 2 : Back Bonding — Effects, Geometry & Comparison

### Key Concepts — Effects of Back Bonding

- Back bonding **can** change hybridisation (e.g. N:  $sp^3 \rightarrow sp^2$  in  $N(SiH_3)_3$ ) but does **not always**
- Bond order **increases**; bond length **decreases**
- Lewis acidity **decreases** (empty orbital gets partially filled)
- Bond angle change: **not always increases** — depends on the specific molecule
- Back bonding strength:  $p\pi-p\pi > p\pi-d\pi$  (period-2 donor is better)
- Shortest B–F bond: free  $BF_3$  (maximum back bonding; no competing Lewis base)

### Q5. Trisilylamine $[N(SiH_3)_3]$ has a

#### Explanation

In a normal amine ( $NR_3$  with C substituents), N is  $sp^3 \Rightarrow$  pyramidal geometry.

In  $N(SiH_3)_3$ : Si has empty  $3d$  orbitals. N's lone pair (in a  $2p$  orbital) overlaps with Si's empty  $3d$  orbital ( $p\pi-d\pi$  back bonding). To maximise this overlap, N **rehybridises from  $sp^3$  to  $sp^2$** : the lone pair moves into a pure  $p$  orbital perpendicular to the N–Si plane, giving much better sideways overlap with Si's  $d$  orbitals.

$sp^2$  N  $\Rightarrow$  **trigonal planar geometry** (all four atoms N, Si, Si, Si in the same plane).

#### Approach

Compare with  $NMe_3$ : C has no  $d$  orbitals  $\Rightarrow$  no back bonding  $\Rightarrow$  N stays  $sp^3 \Rightarrow$  pyramidal. Si has  $d$  orbitals  $\Rightarrow$  back bonding  $\Rightarrow$  N goes flat.

#### Answer

(1) Planar geometry.

### Q6. Which of the following is not possible due to back bonding?

### Explanation

Checking each option:

- (1) *Hybridisation may change* — **True**. e.g. N goes  $sp^3 \rightarrow sp^2$  in  $N(\text{SiH}_3)_3$ .
- (2) *Bond order increases* — **True**. Partial double bond character  $\Rightarrow$  bond order  $> 1$ .
- (3) *Bond angle always increases* — **False/Not always**. Back bonding can increase or may not change the bond angle depending on the molecule. The word “always” makes this statement incorrect.
- (4) *Lewis acidic strength decreases* — **True**. Back bonding partially fills the empty orbital  $\Rightarrow$  less electron-deficient  $\Rightarrow$  weaker Lewis acid.

Only option (3) contains an incorrect claim.

### Approach

The trap word here is “**always**.” In MCQs, watch for absolute words like always/never — they are almost always the wrong statement unless backed by theory.

### Answer

(3) Bond angle always increases — this is **not** always true.

### Q7. In which of the following compounds is the B–F bond length shortest?

#### Explanation

B–F bond length is inversely related to the extent of back bonding. More back bonding  $\Rightarrow$  higher bond order  $\Rightarrow$  shorter bond.

Compound	B hybridisation	Back bonding	B–F bond length
$\text{BF}_4^-$	$sp^3$	None (no empty orbital on B)	Longest
$\text{BF}_3 \leftarrow \text{NH}_3$	$sp^3$	None ( $\text{NH}_3$ fills empty orbital)	Long
$\text{BF}_3 \leftarrow \text{N}(\text{CH}_3)_3$	$sp^3$	None ( $\text{NMe}_3$ fills empty orbital)	Long
$\text{BF}_3$	$sp^2$	<b>Maximum</b> (empty $p$ orbital free)	<b>Shortest</b>

In free  $\text{BF}_3$ , B's  $p$  orbital is completely available for back bonding from all three F atoms  $\Rightarrow$  bond order  $\approx 1.33 \Rightarrow$  shortest B–F bond.

#### Approach

Rule: Anything that donates a lone pair to B kills back bonding and *increases* the B–F bond length. Free  $\text{BF}_3$  = maximum back bonding = shortest bond.

#### Answer

(3)  $\text{BF}_3$  (free, uncoordinated) has the shortest B–F bond.

### Q8. “Hybridisation of central atom does not always change due to back bonding.” This statement is valid for which compounds?

### Explanation

- $\text{CCl}_3^-$ : C is  $sp^3$  (3 bonds + 1 lone pair). Back bonding from Cl  $\rightarrow$  C occurs, but C **remains**  $sp^3$ . Hybridisation **does not change**.
  - $\text{CCl}_2$  (carbene): C is  $sp^2$  (has one empty orbital + one lone pair). Back bonding from Cl donates into C's empty orbital, but C **stays**  $sp^2$ .
  - $\text{CF}_2$  (difluorocarbene): Same as  $\text{CCl}_2$ . C is  $sp^2$  before and after back bonding.
  - $\text{N}(\text{SiH}_3)_3$ : N goes from  $sp^3 \rightarrow sp^2$  due to back bonding — hybridisation **does** change. (validates the “not always” claim via the other three)
- The statement “hybridisation does not always change” is demonstrated as valid by all four compounds taken together, since in three out of four cases the hybridisation *does not* change.

### Approach

The statement says “not always” — not “never.” Even  $\text{N}(\text{SiH}_3)_3$  (where it does change) being in the list is fine, because the statement only says it doesn't happen *always*.

### Answer

(4) All — [ $\text{CCl}_3^-$ ,  $\text{CCl}_2$ ,  $\text{CF}_2$ ,  $\text{N}(\text{SiH}_3)_3$ ].

### Q9. The geometry with respect to the central atom of $\text{N}(\text{SiH}_3)_3$ , $\text{Me}_3\text{N}$ , $(\text{SiH}_3)_3\text{P}$ are:

### Explanation

- $\text{N}(\text{SiH}_3)_3$ : Si has empty  $3d$  orbitals. N's lone pair back-donates ( $p\pi-d\pi$ ). N rehybridises  $sp^3 \rightarrow sp^2$ .  $\Rightarrow$  **Planar**.
- $\text{Me}_3\text{N}$ : C has **no**  $d$  orbitals. No back bonding possible. N stays  $sp^3$ .  $\Rightarrow$  **Pyramidal**.
- $(\text{SiH}_3)_3\text{P}$ : P has  $3p$  lone pair (more diffuse and lower energy than N's  $2p$ ). The energy mismatch between P's  $3p$  and Si's  $3d$  makes back bonding much less effective than in  $\text{N}(\text{SiH}_3)_3$ . P remains essentially  $sp^3$ .  $\Rightarrow$  **Pyramidal**.

### Approach

N is the better back-donor (2nd period,  $2p$  lone pair, good energy match with Si's  $3d$ ). P is a poorer donor (3rd period, energy mismatch)  $\Rightarrow$  P stays pyramidal.

### Answer

(2) planar, pyramidal, pyramidal.

### Q10. In which compound is the observed bond angle greater than expected but not due to back bonding?

### Explanation

- $\text{N}(\text{SiH}_3)_3$ : Bond angle increases to  $120^\circ$  (from expected  $107^\circ$ ) due to back bonding ( $sp^3 \rightarrow sp^2$ ). *This IS due to back bonding.*
- $\text{O}(\text{CH}_3)_2$ : Bond angle  $\approx 111^\circ$  (vs  $104.5^\circ$  in  $\text{H}_2\text{O}$ ). C has no  $d$  orbitals  $\Rightarrow$  **no back bonding**. The larger angle is due to **steric repulsion** of the bulky  $\text{CH}_3$  groups. *Not due to back bonding.* ... but wait:
- $\text{O}(\text{SiH}_3)_2$ : Bond angle  $\approx 144^\circ$  (enormously larger than expected). Si has  $d$  orbitals, so back bonding does occur. However, the primary reason for such a large angle is the **steric repulsion** between the bulky  $\text{SiH}_3$  groups, not back bonding alone. *The angle increase is not primarily due to back bonding.*

The answer is  $\text{O}(\text{SiH}_3)_2$  because its huge observed bond angle ( $\sim 144^\circ$ ) is driven mainly by steric effects of large  $\text{SiH}_3$  groups, not back bonding.

### Approach

Do not confuse “back bonding occurs in a molecule” with “the bond angle change is because of back bonding.” In  $\text{O}(\text{SiH}_3)_2$ , even though back bonding is present, the dominant reason for the angle being so large is the sheer bulk of two  $\text{SiH}_3$  groups pushing each other apart.

### Answer

(3)  $\text{O}(\text{SiH}_3)_2$ .

## ► TYPE 3 : NCERT Based

### Key Concepts — Lewis Acid Behaviour of Group-13 Halides

- Trivalent Group-13 compounds are Lewis acids due to **incomplete octet** (only 6 electrons around the central atom)
- Accepting a lone pair  $\Rightarrow$  hybridisation changes  $sp^2 \rightarrow sp^3 \Rightarrow$  octet completed
- Lewis acid strength of  $\text{BX}_3$ :  $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$  (counter-intuitive: smaller halogen gives more back bonding, reducing Lewis acidity more)
- Down Group 13: atomic size  $\uparrow \Rightarrow$  Lewis acidity  $\downarrow$  (poorer orbital overlap for back bonding, larger  $p$  orbitals less effective)

**Q11.  $\text{BF}_3$  is  $sp^2$ -hybridised. When it accepts  $\text{F}^-$  to form  $\text{BF}_4^-$ , which combination correctly describes the process?**

### Explanation

**Before** ( $\text{BF}_3$ ): B is  $sp^2$ , 3 bond pairs, 6 electrons around B (incomplete octet), empty  $p$  orbital.

**Process:**  $\text{F}^-$  donates a lone pair into B's empty  $p$  orbital.

**After** ( $\text{BF}_4^-$ ): B now has 4 bond pairs  $\Rightarrow sp^3$  hybridisation  $\Rightarrow$  8 electrons around B (complete octet).

This is the definition of **Lewis acid behaviour**: accepting an electron pair from a donor.

### Approach

Lewis acid = electron pair **acceptor**. B had an empty cup ( $sp^2$ ,  $6e^-$ ).  $F^-$  filled it ( $sp^3$ ,  $8e^-$ ). B accepted  $\Rightarrow$  Lewis acid confirmed.

### Answer

(1) Hybridisation changes  $sp^2 \rightarrow sp^3$ , electron count rises  $6 \rightarrow 8$  — confirming Lewis-acid behaviour.

## Q12. Why do trivalent boron compounds such as $BF_3$ behave as Lewis acids?

### Explanation

In  $BF_3$ , B forms three bonds using its three valence electrons. Total electrons around B =  $3 \times 2 = 6$ . The octet requires 8. B has an empty  $p$  orbital and is **electron deficient**. It readily accepts an electron pair from a Lewis base to achieve the stable octet  $\Rightarrow$  Lewis acid.

Options (2), (3), (4) are all wrong:

(2) B does not donate protons (that is Brønsted-Lowry acid behaviour).

(3) B has no lone pair to donate.

(4) Electronegativity of F causes B–F polarity but does not directly cause B to *release* electrons.

### Approach

Octet rule shortcut: count electrons around the central atom. B in  $BF_3 = 6 < 8 \Rightarrow$  electron-deficient  $\Rightarrow$  Lewis acid.

### Answer

(1) Boron has an incomplete octet ( $6e^-$ ) and accepts an electron pair to complete it.

## Q13. A graph: size of Group-13 central atom ( $x$ -axis) vs tendency to accept an electron pair ( $y$ -axis). P = top-left, S = bottom-right. Which point represents the trichloride of the heaviest element?

### Explanation

Down Group 13: atomic size increases ( $B < Al < Ga < In < Tl$ ). Larger atoms have more diffuse, less effective  $p$  orbitals  $\Rightarrow$  poorer overlap with the incoming lone pair  $\Rightarrow$  **weaker Lewis acid**.

**Heaviest element** = largest atom = rightmost on  $x$ -axis = point **S**

**S has lowest  $y$**   $\Rightarrow$  lowest tendency to accept electrons  $\Rightarrow$  weakest Lewis acid.

The curve slopes **downward** left to right  $\Rightarrow$  Lewis-acid strength **decreases** as atomic size increases.

### Approach

Bigger atom = more “spread out” electron cloud around B-analog = less electropositive character = weaker Lewis acid. P (top-left) = smallest atom = strongest Lewis acid. S (bottom-right) = largest atom = weakest Lewis acid.

### Answer

(1) S; Lewis-acid strength **decreases** as atomic size increases.

**Q14.  $\text{AlCl}_3$  is a Friedel–Crafts catalyst. Which trivalent Group-13 chloride would make the weakest such catalyst?**

### Explanation

Friedel–Crafts catalysis requires a strong Lewis acid (ability to accept an electron pair from the substrate).

Down Group 13: Lewis-acid strength decreases with increasing atomic size.

Compound	Central atom	Lewis-acid strength
$\text{AlCl}_3$	Al	Moderate
$\text{GaCl}_3$	Ga	Lower
$\text{InCl}_3$	In	Even lower
$\text{TlCl}_3$	Tl	<b>Lowest</b> (heaviest, largest atom)

$\text{TlCl}_3$  is the weakest Lewis acid  $\Rightarrow$  weakest catalyst.

### Approach

Heaviest element = largest atom = weakest Lewis acid = worst catalyst. Tl is below In in the group, so  $\text{TlCl}_3$  beats  $\text{InCl}_3$  for weakest Lewis acid.

### Answer

(1)  $\text{TlCl}_3$ .

**Q15. Arrange the boron trihalides in increasing order of Lewis-acid strength:**

### Explanation

This is the classic counter-intuitive result of back bonding:

**Expected (by electronegativity alone):**  $\text{BI}_3 < \text{BBr}_3 < \text{BCl}_3 < \text{BF}_3$  (F is most electronegative  $\Rightarrow$  should make B most electron deficient  $\Rightarrow$  strongest Lewis acid).

**Actual order:**  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$

**Reason:** Back bonding partially fills B's empty orbital in each  $\text{BX}_3$ . The extent of back bonding depends on *p*-orbital size match between B and X:

- $\text{BF}_3$ : F is 2nd period; **excellent** *p*–*p* overlap  $\Rightarrow$  strongest back bonding  $\Rightarrow$  empty orbital most

filled  $\Rightarrow$  **weakest** Lewis acid.

- $\text{BI}_3$ : I is 5th period; **very poor** overlap with B's  $2p \Rightarrow$  almost no back bonding  $\Rightarrow$  empty orbital nearly free  $\Rightarrow$  **strongest** Lewis acid.

### Approach

Back bonding fills the "hungry" empty orbital of B. The better the filling ( $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ), the less hungry B is. Less hungry = weaker Lewis acid. So F makes B the least hungry  $\Rightarrow \text{BF}_3$  is the weakest Lewis acid despite F being the most electronegative.

### Answer

(2)  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ .

### Quick Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	(1)	2	(4)	3	(1)	4	(1)	5	(1)
6	(3)	7	(3)	8	(4)	9	(2)	10	(3)
11	(1)	12	(1)	13	(1)	14	(1)	15	(2)