Check Your Progress 2

Notes:1. Write your answers in the space given below.

2. Compare your answers with those given at the end of this unit.

(a). Predict the shape of an H_2O molecule on the basis of a Walsh Diagram for an AB_2 molecule.

(b) Is any AB_2 molecule, in which A denotes an atom of a period 3 element, expected to be linear? If so, which

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1.4 dπ - pπ BONDS.

There are several structural phenomena that have traditionally been attributed to the formation of dπ - pπ Bonds. Recent work has raised some doubts. The phenomena in questions are exemplified by:

1. The fact that for amines such as $(R_3Si)_2$ NCH_3, $(R_3Si)_3$ N and $(H_3Ge)_3$ N, the central NSi_2C, NSi_3 and NGe_3 skeletons are planar.

2. Many tetrahedral species such as SiO_4^{-4}, PO_4^{-3}, SO_4^{-2} and ClO^{-}_4 have bond lengths shorter than those predicted from conventional tables of single bond radii. In silicates the Si-O-Si units also show what were considered to be Si-O distance that are "too short" for single bonds.

Recent re-examinations of these phenomena by both theoretical and experimental methods together with earlier arguments now suggest that the dπ - pπ contributions to these effects are at best small. Thus, in reading literature written prior to 1985, where such interactions are often accorded great importance, one should now be sceptical of all but the facts themselves.

This is not to say that dπ - pπ bonding in main group compounds is never important. Probably in the case of - S - N = S units, and in $F_3F \equiv N$, where the S - N distances are very short indeed. However, it is always dangerous to attribute all structural effects to simple orbital overlaps, even if the explanation seems to fit, and the rise and fall of the dπ - pπ overlap hypothesis is a case in point.

In a multiple bonded molecule having bond pairs + lone pairs = 4, 5 or 6, the π bonds will be pπ - dπ bond. In this case the central atom uses all its p-orbitals for hybridisations and has only d-orbitals available to overlap with p-orbitals of the adjacent atom to give dπ- pπ bond.

The formation of dπ - pπ bond is common for all the second period elements and is not important for the elements of third and higher periods. The pπ-dπ bonding is more favourable than the dπ - pπ bonding for higher atoms of third and higher periods.

1.4.1 dπ - pπ Bonding in Phosphorous Group Elements

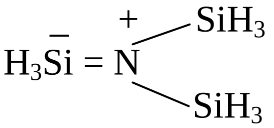
Phosphine Oxide, $R_3P = 0$, presents an important example of the participation of d-atomic orbitals of nonmetallic elements in π bonding. Presence of π bonding is defected with the help of the evidences, such as reduction in the bond length, increase in the bond strength and the stabilisation of charge distribution. On these grounds, compared to ammine oxide, phosphine oxide presents a strong evidence of the presence of dπ - pπ bond, in a very high stability of P = O.

Similarly the fact that almost all t-phosphines are readily oxidised into $R_3P = 0$, also indicates that dπ- pπ bond is present in the P = O bonding. This is supported by the lower dipole moment of triethyl phosphine oxide (1.4×10^{-3} Cm. cf 16.7×10^{-3} Cm. of trimethyl amine oxide), higher dissociation energy of P = O bond (500-600 KJ, cf 200-300 KJ of N→O bond) and the smaller P-O bond lengths in phosphoryl compounds.

1.4.2 dπ-pπ Bonding in Nitrogen, Oxygen and Sulphur Compounds

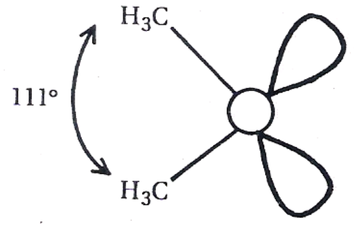
There are number of examples, which show dπ- pπ bonding in nitrogen, oxygen and sulphur compounds:

(i) Mobile π bonding in trisilyl amine results in the resonance in the molecule :

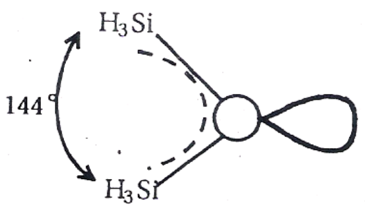


$$H_3\overset{-}{Si} = \overset{+}{N}\begin{matrix} SiH_3 \\ SiH_3 \end{matrix}$$

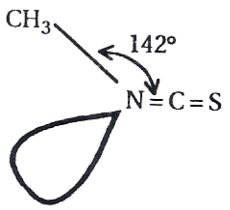
(ii) The bond angles in disiloxane, $H_3SiOSiH_3$, and silyl isothiocyanate, $H_3Si\text{-}N\text{=}C\text{=}S$ indicates pπ - dπ back-bonding (in comparison to ether and methyl isothiocyanate) :



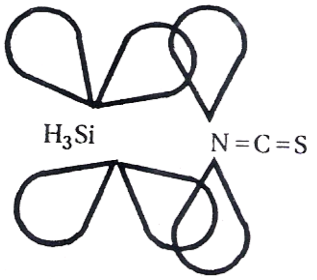
Dimethyl ether
(Sp^3-hybridised. 0 + 2 lp)
Addition compound with BF_3



Disiloxane
(Sp^3-hybridised. 0 + 1 lp)
No addition compound withBF_3



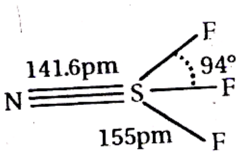
Methyl isothicyanate
(one lp on N; Angular)



Silyl isothiocynate
lp used in π bonding, Linear

The argument given against the use of d atomic orbitals in bonding by non-metallic elements is that a very high excitation energy is required for the same. Hence it may be concluded that the use of d-atomic orbitals in bonding by non-metallic elements will be possible only in their higher oxidation states and when they are linked with strong electronegative elements, eg. PF_5,SF_6,OPX_3 etc.:

(i) The N - S bond length in $N\equiv SF_3$ indicates. The bond order = 2.7 indicating dπ - pπ bonding:

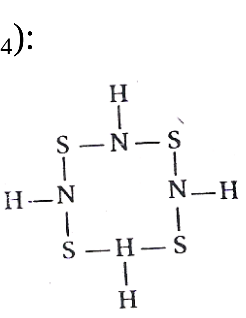


Thiazytrifluoride

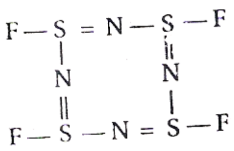
N - S bond length = 141.6 pm; Bond order = 2.7

(cf N - S = 174 pm, b.0 = 1, N = S = 154 pm; b.0 = 2)

(ii) In $S_4N_4F_4$ also there is indication of dπ - pπ bonding (compare with $S_4H_4N_4$):

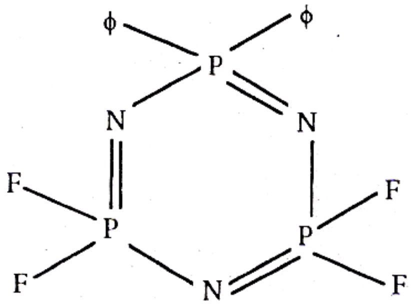


Tetra Sulphur tetramide
(Isoelectronic and
Isomorphous with S_8



Tetra sulphur tetramide fluoride
(Alternate S = N bond)

(ii) In diphenyl phosphonitrilic fluoride, there is evidence of π bonding in the ring:



Check Your Progress-3

Notes: 1. Write your answers in the space given below.

2. Compare your answers with those given at the end of this unit.

(a). In which of the following molecule there is a possibility of dπ-pπ bonding?

$S_4N_4F_4$, $S_4H_4N_4$, $N \cong SF_3$, $H_3SiOSiH_3$, $CH_3N = C=S$ and Et_3NO.

Ans: (i) ------------------------------ (ii)----------------------

(iii) -----------------------------

(b) Which are the evidences in favour of dπ-pπ bonding in R_3PO molecule?

Ans: (i) ---------------------------------

(ii) --------------------------------

(iii) -------------------------------