Inorganica Chimica Acta, 13 (1975) 121–125

The Electronic Structure of Difluorophosphine, Difluorophosphine Oxide, and Difluorophosphine Borane

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Received July 16, 1974

The electronic structures of difluorophosphine (HPF_2), difluorophosphine oxide (HPF_2O), and difluorophosphine borane ($HPF_2 \cdot BH_3$) are examined by a non-empirical calculational procedure. The calculations reveal that the role of the d orbitals of phosphorus is important for HPF_2O while their participation in the bonding of HPF_2 and $HPF_2 \cdot BH_3$ is still significant. The tilting of the BH_3 group within $HPF_2 \cdot BH_3$ is found to stabilize the molecule by 8.41 kJ mol^{-1}. The barrier to rotation about the P–B bond for $HPF_2 \cdot BH_3$ is calculated to be 23.09 kJ mol^{-1} in good agreement with experiment. In the eclipsed configuration of $HPF_2 \cdot BH_3$, the BH_3 moiety occupies a non-tilted position. The energies of formation of $PH_3 \cdot BH_3$, $HPF_2 \cdot BH_3$, and $PF_3 \cdot BH_3$ are calculated and the order of stability of these compounds is $HPF_2 \cdot BH_3 > PF_3 \cdot BH_3 > PH_3 \cdot BH_3$ which agrees with experiment. Reasons are presented for the position of $HPF_2 \cdot BH_3$ in this sequence.

Introduction

Difluorophosphine borane ($HPF_2 \cdot BH_3$) has attracted a lot of attention ever since it was realised that it was quite stable at room temperature.[1] This is in complete contrast to the related compounds, $F_3P \cdot BH_3$ and $H_3P \cdot BH_3$, which are highly dissociated at NTP. Recent structural investigations[2] revealed two additional intriguing features. First, the borane group is tilted away from the fluorine atoms so that the two PBH angles differ by approximately 10°. Second, the molecule adopts a staggered conformation with an estimated barrier to rotation of 15.06–18.83 kJ mol^{-1} about the P–B bond. This rotational energy is high in comparison with the estimated barrier of 9.64 kJ mol^{-1} and 0.37 kJ mol^{-1} about the related B–N bond of $BH_3 \cdot NH_3$[3] and $BF_3 \cdot NH_3$[3] respectively. As the P–B and N–B bond differ mainly through the substitution of phosphorus $3p$ for nitrogen $2p$ orbitals and through the possible participation of $3d$ orbitals of phosphorus in the former, it is suggested that these are involved in π-bonding across the P–B bond and so are a hindrance to rotation. It is not permissible, however, to invoke the $3d$ orbitals of phosphorus as the reason for either the stability of $HPF_2 \cdot BH_3$ or the tilt of the borane group, as $PF_3 \cdot BH_3$ would also be expected to have similar properties. The only obvious difference between these complexes is the presence of a P–H bond in $HPF_2 \cdot BH_3$. Hence interaction of this hydrogen with the borane group might be considered to bestow extra stability or the molecule. Therefore an *ab initio* investigation into the electronic structures of $HPF_2 \cdot BH_3$ and its components HPF_2 and BH_3 was initiated to provide information about its unusual features. Calculations were also performed on difluorophosphine oxide (HPF_2O), isoelectronic with $HPF_2 \cdot BH_3$, in order to compare the two different types of Lewis acid-Lewis base interactions and furthermore to examine the hydrogen–oxygen bonding for manifestations of a reactive hydrogen atom. Previous calculations on $HPF_2 \cdot BH_3$ have been semi-empirical[4] and empirical[2] in nature.

The calculations were performed within the usual LCAO–MO–SCF framework in which the atomic orbitals are represented by linear combinations of gaussian functions. The $13s$ and $9p$ primitive gaussian functions of phosphorus are contracted to give $6s$ and $4p$ orbitals[5], while for boron, fluorine and oxygen we combine the $9s$ and $5p$ gaussian functions to produce $4s$ and $2p$ atomic orbitals[6]. Four s functions contracted to two atomic orbitals simulate the $1s$ orbitals of hydrogen[6]. The $3d$ orbitals of phosphorus were represented by a linear combination of three gaussian functions chosen to reproduce a Slater type $3d$ orbital[7]. Preliminary calculations were performed to obtain an optimum Slater exponent for the $3d$ orbitals of phosphorus in HPF_2. This exercise yielded 1.8 for the orbital exponent which was then used in the subsequent calculations. The structural information of the molecules was extracted from references 2, 8, 9 and 10.

The Electronic Structure of HPF_2

The gross atomic and overlap populations of HPF_2, HPF_2O, BH_3 and $HPF_2 \cdot BH_3$ are presented in Table I.

TABLE I. The Atomic and Overlap Populations of HPF_2, HPF_2O, $HPF_2 \cdot BH_3$ and BH_3.

Gross Atomic Populations

	HPF_2	HPF_2O	$HPF_2 \cdot BH_3$	BH_3
P				
s	5.63	4.99	5.32	–
p	8.18	7.89	8.19	–
d	0.42	0.92	0.59	–
total	14.23	13.79	14.10	–
F				
s	3.94	3.93	3.94	–
p	5.50	5.46	5.46	–
total	9.44	9.39	9.40	–
B				
s	–	–	3.08	3.12
p	–	–	2.40	1.96
total	–	–	5.48	5.08
O				
s	–	3.84	–	–
p	–	4.72	–	–
total	–	8.56	–	–
H_P *s*	0.90	0.84	0.83	–
H_{B1} *s*	–	–	0.91	0.97
H_{B2} *s*	–	–	0.94	0.97
H_{B3} *s*	–	–	0.94	0.97

Overlap Populations

	HPF_2	HPF_2O	$HPF_2 \cdot BH_3$	BH_3
H_P–P	0.64	0.78	0.74	–
F–P	0.42	0.58	0.50	–
H_P–O	–	–0.04	–	–
O–P	–	1.30	–	–
H_P–B	–	–	–0.04	–
P–B	–	–	0.36	–
B–H_{B1}	–	–	0.84	0.82
B–H_{B2}	–	–	0.82	0.82

In HPF_2 the phosphorus atom possesses a large positive charge due to donation of its valence electrons, mainly π-electrons, to the fluorines. The electrons of hydrogen are relatively unpolarised bestowing a small positive charge on the atom. A breakdown of the bond overlap populations reported in Table I reveals the nature of the bonding in the molecule. The P–H bond is largely composed of the phosphorus p σ-hydrogen s contribution (92%). The P_d–H_s component is small while the P_s–H_s content is antibonding. Similar features are present in the P–F bonds where the phosphorus s orbital is only slightly involved in the bonding. The p and d orbitals of phosphorus, however, form strong bonds with the fluorine p orbitals. Close inspection of the wave function reveals that the π-bonding content is substantial. The highest filled orbital is largely localised on the s and p orbitals of phosphorus representing the classical picture of a lone pair of electrons in a sp^3 hybrid. The main contribution to the first vacant orbital is a p orbital of the phosphorus perpendicular to the plane incorporating the P–H bond and bisecting the FPF angle.

The Electronic Structure of HPF_2O

From the results of Table I we can observe the electronic distribution changes that have occurred as HPF_2 forms an oxide. The outcome is a large electron drift (0.56) towards oxygen from the HPF_2 group. The main source of the donated electrons is the phosphorus atom although the hydrogen and the two fluorines have also lost a small amount of electron density. It is interesting to note that this electron release has brought about an increase in the P–H and P–F bond populations due to increased participation in these bonds by the s and d orbitals of phosphorus. The P–O bond has a large overlap population emanating from interaction of the oxygen p orbitals with the phosphorus orbitals. The π-bond contribution, especially the P_d–O_p component is a substantial part of the P–O bond. This component is also the cause of the increase in the electron π density of the phosphorus d orbital through back bonding with oxygen. The intramolecular O–H bond is weakly antibonding.

The Electronic Structure of $HPF_2 \cdot BH_3$

The important feature of the electronic structure of $HPF_2 \cdot BH_3$ is a donation of 0.27 electrons to the BH_3 moiety. These released electrons stem largely from the phosphorus 3*s* orbital with a small amount from the hydrogen s and fluorine p orbitals. The borane group shows some interesting changes through coordination to HPF_2. The boron p orbitals have gained electrons while the s orbital population has diminished. The biggest orbital population change occurs in the boron p orbital which is vacant in planar BH_3 and is now occupied by 0.4 electrons. The hydrogen which is tilted towards the HPF_2 has gained electron density while the two hydrogens which are inclined away from the difluorophosphine have been deprived of electronic charge. The B–P bond consists of two large bonding components, namely P_s–B_p and P_p–B_p, coupled with an antibonding P_s–B_s constituent. The π-bonding is not as important as it is in the P–O bond of HPF_2O and accounts for ~20% of the P–B overlap population. Coordination has caused a strengthening of the B–H bonds, the F–P bonds, and the H–P bonds.

From the orbital population data we can conclude that d orbital participation is important for HPF_2O while its role in the bonding in HPF_2 and $HPF_2 \cdot BH_3$ is still significant. This is also reflected in the changes in calculated total energies of the molecules when the d orbitals of phosphorus are omitted from the basis set. The resulting increase in energy of HPF_2, $HPF_2 \cdot BH_3$ and HPF_2O is 288.2 kJ mol^{-1}, 375.6 kJ mol^{-1}, and 602.9 kJ mol^{-1}, respectively.

The Electronic Structure of Non-tilted $HPF_2 \cdot BH_3$

So far, nothing has emerged from the above calculations which can explain the tilting of the borane moiety within $HPF_2 \cdot BH_3$. It was therefore necessary to obtain the electronic energies and orbital populations of $HPF_2 \cdot BH_3$ in which BH_3 has C_3 symmetry with respect to the B–P axis. It was found (Table II) that the loss in stability due to adopting a non-tilting configuration is 8.41 kJ mol^{-1}. The tilted configuration has a lower nuclear energy and although the non-tilted structure has a more negative electronic energy, the nuclear energy change was the more dominant.

There is very little difference in the orbital populations of the two configurations. The main change is a small increase in the population of the hydrogens of the borane unit and a concomitant loss in electron density by the boron *p* orbitals. The non-tilted configuration displays an increase in the overlap populations of the P–B and P–F bonds in alliance with the more negative electronic energy. Perhaps the most interesting point to emerge from the overlap population data is that the overlap populations of all the bonds involving the hydrogens are larger in the tilted configuration. The most notable increase occurs in the P–H_{B1} bond where H_{B1} is the hydrogen tilted away from the HPF_2 group. In a similar fashion the B–F bond is less antibonding in the tilted configuration.

In conclusion, we can state that the tilting of the borane group produces a decrease in the nuclear energy because the distortion is directed away from the fluorine atoms. At the same time, tilting causes an increase in the electronic energy and this is manifest in decreased overlap populations of the P–B and P–F bonds. However, there is an increase in bond populations involving the hydrogen atoms and the B–F bonds' population and this causes the electronic energy changes to be smaller than the nuclear energy changes.

Energy of Rotation about the P–B Bond

The eclipsed configuration of $HPF_2 \cdot BH_3$ was calculated and the resulting energies and electronic popu-

TABLE II. The Electronic Energies and Populations of the Staggered and Eclipsed Configurations of $HPF_2 \cdot BH_3$.

	Staggered		Eclipsed	
	BH_3 tilted	BH_3 non-tilted	BH_3 tilted	BH_3 non-tilted
Electronic Energy	–751.78976	–752.36735	–752.72899	–752.47340
Nuclear Energy	185.16306	185.74384	186.11669	185.85551
Total Energy	–566.62670	–566.62351	–566.61230	–566.61789
Gross Atomic Populations				
P	14.100	14.092	14.070	14.072
B	5.486	5.462	5.508	5.513
F	9.402	9.402	9.400	9.400
H_{B1}	0.909	0.921	0.943	0.935
H_{B2}, H_{B3}	0.938	0.944	0.919	0.921
H_P	0.837	0.832	0.842	0.840
Overlap Populations				
P–F	0.504	0.520	0.508	0.508
P–B	0.358	0.450	0.490	0.446
P–H_P	0.782	0.750	0.734	0.736
B–H_{B1}	0.840	0.832	0.812	0.824
B–H_{B2}	0.816	0.808	0.810	0.804
B–H_p	–0.034	–0.040	–0.052	–0.048
P–H_{B1}	–0.080	–0.126	–0.110	–0.108
P–H_{B2}	–0.086	–0.100	–0.198	–0.152
F–H_{B1}	0.0002	0.0010	–	–
H_{B3}–H_P	–0.0006	0.0010	–	–
H_P–H_{B1}	–	–	0.0008	–0.0006
H_{B2}–F_1	–	–	0.0002	–0.0008
H_{B3}–F_2	–	–	0.0026	0.0022
B–F	–0.008	–0.010	–0.016	–0.014

lations are presented in Table II. The energy of rotation about the P–B bond is computed to be 37.78 kJ mol^{-1} which is high in comparison with the experimental value. However it must be remembered that in this particular eclipsed form, the tilting of the BH_3 group might not attain the extra stability that is found in the staggered configuration. Therefore the energy and electronic structure of the eclipsed form of the non-tilted $HPF_2 \cdot BH_3$ molecule were obtained. It was found (Table II) that the latter configuration is more stable than the eclipsed tilted conformation by 14.69 kJ mol^{-1}. The barrier to rotation about the P–B bond is therefore 23.09 kJ mol^{-1} in good agreement with the observed value.

The dominating energy term which determines the preferred eclipsed configuration is the nuclear energy contribution. The tilted-eclipsed configuration of $HPF_2 \cdot BH_3$ has a more negative electronic energy but possesses larger antibonding interactions involving the hydrogen atoms and between the boron and fluorine atoms than is observed in the preferred non-tilted configuration.

It is now possible to compare the electronic changes which occur on rotation about the P–B bond. The phosphorus and fluorine atoms lose electron density while the boron atom becomes more negatively charged. However, it is the hydrogen atoms which display the most change. Both the hydrogen bonded to phosphorus gain electron density on rotation, while the remaining two hydrogen atoms release electrons during transformation to the eclipsed configuration. In general, rotation about the P–B bond causes the overlap population of the P–B and P–F bonds to increase while the remaining bonds suffer a loss. This decrease is particularly marked in the interactions between the borane hydrogens and phosphorus and for boron–fluorine bonds.

Energy of Formation of $HPF_2 \cdot BH_3$

In order to confirm the aforementioned sequence of stabilities of $HPF_2 \cdot BH_3$, $H_3P \cdot BH_3$, and $F_3P \cdot BH_3$, the energies of formation (ΔE_f) were calculated for the reaction.

$^1/_2\ B_2H_6 + H_xPF_{3-x} \rightarrow H_xPF_{3-x} \cdot BH_3$

for x = 0, 1, and 3. The molecular dimensions of the molecules were taken from reference 2. It was found that ΔE_f values for x = 0, 1, and 3 are +18.74 kJ mol^{-1}, –15.19 kJ mol^{-1} and +41.06 kJ mol^{-1} respectively. These figures confirm that the order of stability is $HPF_2 \cdot BH_3 > F_3P \cdot BH_3 > H_3P \cdot BH_3$. It must be remembered that the above value is only one of many energy terms which constitute the free energy of reaction. It is thought that the stability sequence will not be altered by the inclusion of these terms but merely a change in absolute value of the energy terms will occur.

It has been suggested that the energy of reorganising the fluorophosphines into a configuration suitable for bonding to the borane may be a crucial factor in determining the relative stabilities of the borane complexes. Hence the energies of HPF_2 and PF_3 were recalculated using the coordinate system obtained for $HPF_2 \cdot BH_3$ and $PF_3 \cdot BH_3$. This reorganisation involves contraction of the bond lengths and expansion of the inter-bond angles. The energy for such a transformation is 10.92 kJ mol^{-1} and 7.38 kJ mol^{-1} for PF_3 and HPF_2 respectively. Although the reorganisation energy is favourable for HPF_2 it is clearly not the dominating factor in determining the order of stability.

The energies of the highest filled and lowest empty orbitals of PF_3, HPF_2, and PH_3 along with the corresponding orbitals for their borane complexes are presented in Table III. It can be seen that HPF_2 has the lowest-lying vacant orbital while only PH_3 has a higher filled orbital than difluorophosphine. It is generally accepted that these orbitals play an important role in the formation of donor–acceptor complexes. Hence from a consideration of these orbital values, HPF_2 would certainly appear to be a better Lewis base than either PH_3 or PF_3. Moreover, when we examine the orbital values for the borane complexes we find that the stabilisation of the highest filled orbital due to complexing is greatest for HPF_2.

The electronic distribution of $H_3P \cdot BH_3$ and $F_3P \cdot BH_3$ were examined in order to rationalise the calculated energies of formation and the relevant information is listed in Table III. The electron density results reveal that there is an electron donation towards the borane unit of 0.28 e, 0.27 e, and 0.25 e for $H_3P \cdot BH_3$, $HPF_2 \cdot BH_3$, and $PF_3 \cdot BH_3$ respectively. For $PH_3 \cdot BH_3$ the source of this density is the phosphine hydrogen atoms while the *s* orbital population of phosphorus in PF_3 suffers the greatest loss upon complexing to BH_3. The electron transfer process for $HPF_2 \cdot BH_3$ is not too unexpectedly a hybrid of these two effects. The formation of the borane complexes increases the *d* orbital population of the phosphorus atom and this increase can be correlated with the decrease in the borane hydrogen population, the P–B bond population, and the number of fluorine atoms. Therefore it might be expected that $F_3P \cdot BH_3$ would be the most stable complex. The reversal of order of stability for $HPF_2 \cdot BH_3$ and $PF_3 \cdot BH_3$ must be due to the more antibonding long range forces present in the latter complex *e.g.* the B–F and P–H_B bonds (Table III). Substitution of a fluorine atom in $PF_3 \cdot BH_3$ by a hydrogen atom, with the subsequent tilting of the BH_3 group, causes a decrease in these interactions with a concomitant increase in the stability of $HPF_2 \cdot BH_3$.

In conclusion we can state that the order of stabilities, $HPF_2 \cdot BH_3 > F_3P \cdot BH_3 > H_3P \cdot BH_3$ is due to several factors. The presence of fluorine atoms bonded

TABLE III. The Electronic Distributions and Selected Orbital Energies of PH_3, PF_3, HPF_2, $PH_3 \cdot BH_3$, $PF_3 \cdot BH_3$, and $HPF_2 \cdot BH_3$.

	PH_3	HPF_2	PF_3	$PH_3 \cdot BH_3$	$HPF_2 \cdot BH_3$	$PF_3 \cdot BH_3$
Molecular Orbital Energies						
Highest filled (au)	−0.373	−0.419	−0.477	−0.400	−0.476	−0.502
Lowest empty (au)	−0.168	0.137	0.141	0.118	0.130	0.145
Atomic Orbital Populations						
P *s*	5.78	5.63	5.58	5.63	5.32	5.16
p	9.38	8.18	7.65	9.36	8.19	7.73
d	0.17	0.42	0.52	0.25	0.59	0.72
total	15.33	14.23	13.75	15.24	14.10	13.61
F *s*	–	3.94	3.94	–	3.94	3.94
p	–	5.50	5.48	–	5.46	5.45
total	–	9.44	9.42	–	9.40	9.39
B *s*	–	–	–	3.02	3.08	3.11
p	–	–	–	2.45	2.40	2.39
total	–	–	–	5.47	5.48	5.50
$H_{B1}s$	–	–	–	0.94	0.91	0.92
$H_{B2,\,B3}s$	–	–	–	0.94	0.94	0.92
$H_P s$	0.89	0.90	–	0.82	0.83	–
Overlap Populations						
P–B	–	–	–	0.286	0.358	0.382
P–F	–	0.422	0.455	–	0.504	0.562
P–H_P	0.659	0.647	–	0.702	0.782	–
B–H_{B1}	–	–	–	0.808	0.840	0.824
B–H_{B2}	–	–	–	0.808	0.816	0.824
P–H_P	–	–	–	−0.022	−0.034	–
B–H_{B1}	–	–	–	−0.009	−0.080	−0.105
P–H_{B2}	–	–	–	−0.009	−0.086	−0.105
H_{B2}–H_P	–	–	–	−0.002	−0.0006	–
H_{B1}–F_1	–	–	–	–	0.0002	−0.0002
B–F	–	–	–	–	−0.008	−0.010

to the phosphorus atom ensures that there is a strong P–B bond formed between the phosphine and borane groups. The greater stability of the difluoro derivative over the trifluorophosphine complex stems from smaller antibonding interactions present in $HPF_2 \cdot BH_3$, a lower reorganisation energy of HPF_2, and more favourable orbital energies of HPF_2.

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