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The Electronic Structures of Some van der Waals Complexes of Boron Trifluoride

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The electronic structures and energies of three van der Waals complexes of boron trifluoride namely $N_2\cdot BF_3$, $OC\cdot BF_3$ *and* $Ar\cdot BF_3$ *are reported. The calculated energies of complexing of these molecules are small: 4.07, 4.34 and 0.01 kcal* mol^{-1} *for* $N_2\cdot BF_3$, $OC\cdot BF_3$ *and* $Ar\cdot BF_3$ *respectively. In the formation of these complexes a small amount of electrons* ($\leqslant 0.03$) *is transferred to the* BF_3 *species and the resulting coordination bond population* ($\leqslant 0.06$) *is weak. Dipole moment calculations indicate that in* $OC\cdot BF_3$ *the* BF_3 *moiety is distorted out of the plane by 4° while in* $Ar\cdot BF_3$ *and* $N_2\cdot BF_3$ *a planar configuration of* BF_3 *is present.*

Introduction

Molecular clusters of boron trifluoride are formed when a mixture of the reacting species is expanded through a supersonic nozzle [1, 2]. The microwave spectra of three of these van der Waals complexes $Ar\cdot BF_3$, $N_2\cdot BF_3$, and $OC\cdot BF_3$ have been recorded and yield interesting structural data about the complexes [2]. The molecules are symmetric tops with the BF_3 moiety only slightly distorted out of plane by one degree upon bond formation. The measured coordination bond lengths, B–Ar = 3.334 Å, B–N = 2.864 Å and B–C = 2.886 Å, are longer than the expected sum of covalent radii and they can only be rationalised as a sum of van der Waals radii. We accordingly estimate that the van der Waals radius for BF_3 is approximately 1.3–1.4 Å. The recorded dipole moments of the three molecules are 0.178 D, 0.35 D and 0.592 D for $Ar\cdot BF_3$, $N_2\cdot BF_3$ and $OC\cdot BF_3$ respectively [2]. These values are indicative of a charge transfer as the BF_3 unit is only slightly distorted out of the plane. Therefore it would be of interest to obtain a measure of the electron donation involved in these van der Waals complexes as well as to acquire a value for the energies of coordination expected for these weak complexes of BF_3. The electronic structures of various ionic and covalent donor–acceptor complexes of BF_3 have been detailed [3, 4] and so comparison may be valuable.

Calculational Method

The calculational framework incorporated a non-empirical version of the LCAO–MO–SCF method. The basis orbitals for the first row atoms were composed of a (9*s*, 5*p*) set of primitive gaussian functions suitable contracted via the Dunning procedure [5] to give a double-zeta basis set (4*s*/2*p*). For argon a (13*s*, 9*p*) set of gaussian functions [6] was contracted in a similar manner to give the double zeta basis set (6*s*/4*p*) and this was augmented by a set of single-zeta gaussian 3*d* orbitals.

The geometry of each molecule was constructed from the structural information given above and from reference 7.

Results and Discussion

Initially it was necessary to obtain an exponent for the 3*d* gaussian orbitals of argon. This was achieved by using an energy minimisation procedure on $Ar\cdot BF_3$ and an optimised exponent of 0.14 was obtained. The low value for the exponent can be related to the long B–Ar bond distance present in the complex. The variation of the total energy, dipole moment and the argon 3*d* orbital population of $Ar\cdot BF_3$ with the 3*d* orbital exponent of argon is presented in Table I. The argon 3*d* orbitals have a negligible population and this is reflected in the small energy changes obtained in the variation procedure. Indeed, inclusion of the 3*d* orbitals on argon produced a lowering in the total energy of only 0.31 kcal mol^{-1}. However, the changes in the dipole moment are not negligible and we observe an increase in the dipole moment as we decrease the 3*d* orbital exponent from 0.80 to 0.20. Further reduction in the exponent, however, results in a decrease in the dipole moment.

The electronic energies of the three complexes are included in Table II. The coordination energy of these species is low and indicates that the three complexes are likely to be obtained only in procedures similar to the one reported in reference 1. It is

TABLE I. The Variation of the Total Energy, 3*d* Orbital Population and Dipole Moment of $Ar \cdot BF_3$ with the Ar 3*d* Gausian Orbital Exponent.

Ar 3*d* Orbital Exponent	Total Energy of $Ar \cdot BF_3$ (a.u.)	Ar 3*d* Orbital Population	Calculated Dipole Moment (D)
0.80	–849.940186	0.0001	0.275
0.60	–849.940237	0.0001	0.304
0.40	–849.940341	0.0002	0.331
0.20	–849.940537	0.0013	0.348
0.17	–849.940565	0.0016	0.341
0.16	–849.940572	0.0018	0.338
0.15	–849.940577	0.0021	0.333
0.14	–849.940579	0.0022	0.327
0.13	–849.940578	0.0024	0.320
0.10	–849.940548	0.0031	0.292
No 3*d* orbitals	–849.940085	–	0.233

TABLE II. The Electronic Energies of Three Complexes of BF_3.

	Total Energy of Complex (a.u.)	Sum of Total Energies of Donor and BF_3 (a.u.)	Energy of Coordination (kcal mol^{-1})
$N_2 \cdot BF_3$	–432.04194	–432.03545	–4.07
$OC \cdot BF_3$	–435.84916	–435.84224	–4.34
$Ar \cdot BF_3$	–849.94058	–849.94056	–0.01

TABLE III. The Atomic Charges, Overlap Populations and Dipole Moments of Three Complexes of BF_3.

	Atomic Charges				Electrons Transferred to BF_3	Bond Populations			Dipole Moment (D)	
$X{-}Y \cdot BF_3$	X	Y	B	F		X–Y	Y–B	B–F	Calc.	Expt.
$N_2 \cdot BF_3$	–0.007	+0.036	+0.875	–0.301	0.029	1.140	0.058	0.638	0.53	0.35
$O{-}C \cdot BF_3$	–0.193	+0.217	+0.886	–0.303	0.024	1.232	0.051	0.634	0.10	0.59
$Ar \cdot BF_3$	–	+0.005	+0.883	–0.296	0.005	–	0.014	0.640	0.33	0.18
N–N	0.0	0.0	–	–	–	1.160	–	–	–	–
O–C	–0.215	+0.215	–	–	–	1.168	–	–	–	–
BF_3	–	–	+0.885	–0.295	–	–	–	0.638	–	–

interesting to note that only a small range of the Ar 3*d* exponent (0.11–0.18) produces a total energy of $Ar \cdot BF_3$ which is more stable than the sum of the energies of Ar and BF_3. Argon, along with other members of the noble gases, is used as a constituent of an inert matrix in matrix isolation work. It is obvious from this work that argon is a reasonable choice for this type of experiment.

The electronic populations of the complexes and their components are given in Table II. In all three complexes, the amount of electron density transferred to the BF_3 moiety and the value of the overlap population of the coordinated bond is small. Comparison with the corresponding values for $H_3N \cdot BF_3$ where 0.27 electrons are transferred and the B–N overlap population is 0.18 [3] illustrates the weak nature of the three complexes.

For all three complexes the donated electrons are smeared over the π orbitals of BF_3. The transferred electrons of $N_2 \cdot BF_3$ originate on the nitrogen $p\sigma$ orbitals and we observe a loss in the N–N overlap population upon complexing. In the case of $OC \cdot BF_3$, the oxygen atom loses 0.022 electrons upon coordination in the form of a π-electron shift to the carbon atom. The population of the carbon 2*s* orbital is decreased by electron transfer to the BF_3 moiety. This multi-displacement of electrons produces an increased C–O overlap population and this rationalises the fact that $OC \cdot BF_3$ has a greater coordination energy than $N_2 \cdot BF_3$ even though the latter has the larger overlap population for the coordination bond and a greater transfer of electronic change. In $Ar \cdot BF_3$ the donated electrons stem from the argon $3p\sigma$ orbital.

The calculated and experimental dipole moments of the three complexes are in reasonable agreement considering that we used a non-optimised set of B–F, N–N and C–O bond lengths for the complexes. The angle of the BF_3 plane distortion could be in error by 1–3° [2] and it was decided to alter the angle of distortion by this value and investigate the variation of the dipole moment. Better agreement with the experimental dipole moments is obtained by decreasing the angle of distortion to 0° for $N_2 \cdot BF_3$ and $Ar \cdot BF_3$ and by increasing the angle to 4° for $OC \cdot BF_3$. The resulting dipole moments are 0.37 D ($N_2 \cdot BF_3$), 0.18 D ($Ar \cdot BF_3$) and 0.62 D ($OC \cdot BF_3$). Therefore, it seems probable that the above geometries are adopted by the complexes.

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