The molecular complexes of boron trifluoride with nitrosyl fluoride and nitrosyl chloride. Ion-pair formation

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HIGHLIGHTS

- Some properties of six complexes formed between BF_3 and ONF or ONCl are presented.
- These properties are the structures, interaction energies and vibrational spectra.
- Two of the complexes are neutral and four are ion pairs.
- The interaction energies of the two groups of complexes differ by a factor of about 25.

ARTICLE INFO

ABSTRACT

The electron donor–acceptor complexes formed between boron trifluoride and the nitrosyl halides ONF and ONCl have been studied by means of *ab initio* molecular orbital theory at the second order level of Møller–Plesset perturbation theory and with Dunning's augmented correlation-consistent polarized valence triple-zeta basis set. The focus of the calculations was on the structures, interaction energies and vibrational spectra of the complexes. A variety of trial structures were examined, with electron donation occurring from the oxygen, nitrogen and halogen atoms, in an attempt to establish the most favorable site for interaction. In addition, a number of rotational isomers for each adduct were investigated. It was found that, in both cases, the halogen atom was the preferred donor atom. Several of the optimized structures suggested that the formation of ion pairs would lead to stable complexes, and four separate ion-pair structures were included among the possible associated species for each combination of interacting molecules. In those cases the computed spectra were more consistent with those of the NO^+ and BF_4^- or $BClF_3^-$ ions than of the corresponding neutral components. The relative stabilities of the two families of complexes have been rationalized and some differences between the properties of the ONF and ONCl adducts have been observed and explained.

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Introduction

Boron trifluoride is often regarded as a prototypical Lewis acid, and forms stable complexes with a wide variety of bases containing nitrogen, oxygen and halogen, among other atoms. A large number of gas-phase spectroscopic and electron diffraction publications on such complexes have been collated in the bibliography of Novick [1], and a recent review by Young has reported on the vibrational spectra of these adducts studied by the matrix isolation technique [2]. Moreover, a recent publication from this laboratory has reviewed the wealth of data provided by *ab initio* theoretical studies on boron trifluoride complexes [3]. In most cases the site of electron donation is easily predicted, particularly if the base

contains only one electronegative atom. Where there is the possibility of competition between two (or more) potential electron donor atoms, however, the prediction of the most probable interaction site is less easy. For example, the complex formed between boron trifluoride and hydroxylamine was shown to be preferentially bound through the $2sp^3$ hybridized nitrogen atom, rather than the $2sp^3$ hybridized oxygen [4]. Similarly, the boron trifluoride-nitrous acid complex has three distinct possible sites of interaction, and the order of stability of the adducts bound through the various sites is hydroxyl oxygen ($2sp^3$) > nitrogen ($2sp^2$) > nitrosyl oxygen ($2sp^2$) [3]. The nitrosyl halides ONF and ONCl provide an opportunity to determine the relative abilities of the nitrogen, oxygen and halogen atoms to engage in complex formation and, further, to weigh the donor properties of fluorine and chlorine atoms against each other.

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The matrix isolation spectra of boron trifluoride complexes have been referred to above [2], and those of nitrosyl chloride species have been reported by Jones and Swanson [5] and Schriver-Mazzuoli et al. [6] (monomer and dimer), Sanna et al. [7] (complex with HCl), Hallou and co-workers [8] (complex with H_2O), Bai and Ault [9] (complexes with oxygen-, sulfur-, selenium- and π-donors), and Hallou and co-workers [10] (photo-induced interconversion of ONCl and ClON). In addition, the dimers $(ONF)_2$ and $(ONCl)_2$ have been studied *ab initio* by Ford et al. [11]. However, the existence of complexes of BF_3 with either ONF or ONCl does not seem to have been established experimentally, either in the gas phase or in cryogenic matrices.

In this paper we explore theoretically the properties of the complexes of boron trifluoride with nitrosyl fluoride and chloride, in an attempt to locate the minimum energy structures of each interacting pair, and to estimate the relative interaction energies of the stable adducts.

Computational methodology

The calculations were performed using the Gaussian-09 program [12], at the second order level of Møller–Plesset perturbation theory (MP2) [13] and with the augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ) of Dunning *et al.* [14–17]. Geometry optimizations were undertaken at the tight convergence level [12], where practical. Harmonic vibrational analyses were carried out. The interaction energies were calculated using the energies of the complexes and of the relaxed monomers, and were corrected for basis set superposition error (BSSE) [18], using the full counterpoise technique of Boys and Bernardi [19], and for vibrational zero-point energy differences. The major molecular orbital interactions were identified and the atomic charges computed using natural bond orbital (NBO) theory [20], employing the NBO Version 3.1 feature of Gaussian-09 [21].

Results and discussion

Molecular structures and interaction energies

A total of ten starting structures were examined for each interacting base. These structures included four oxygen-bound, two nitrogen-bound and four halogen-bound adducts in each case. The oxygen-bound and halogen-bound species were interrelated by the dihedral angles around the B···O and NO, and the B···X and NX bonds (X = F, Cl), and the nitrogen-bound complexes by

rotation about the B···N bonds. The ten starting structures for the BF_3·ONF complexes are illustrated in Fig. 1; those for the ONCl analogues are qualitatively similar. Of these starting structures, three each of the ONF and ONCl families optimized to yield genuine minima. In the case of BF_3·ONCl, the Cl-bound (**11**) and N-bound (**12**) isomers were found to be neutral complexes. These structures are illustrated in Fig. 2. In contrast to the point group of structure (**12**), which is C_s, that of (**11**) is C_1; this is because the electrostatic repulsion of the F3 and O7 atoms is relieved if the O7 atom is displaced from the F3B1Cl2N6 plane. A third complex (**16**) is more accurately described as an ion pair, resulting from heterolytic breaking of the NCl bond to form NO^+ and $BClF_3^-$ ions. The three ONF complex structures (**13**), (**14**) and (**15**) were also found to be more consistent with ion pairs, with breaking of the NF bonds to form NO^+ and BF_4^- ions. The structures of these ion pairs are shown in Fig. 3, and all four belong to the C_s point group.

The interaction energies of the six complexes, corrected for basis set superposition error and for zero-point energy differences, are collected in Table 1. Those of the two neutral complexes are modest (less than -20 kJ mol^{-1}), and the chlorine-bound isomer of BF_3·ONCl (**11**) is significantly more strongly bound than the N-bound analogue (**12**). The interaction energies of the ion-pair complexes are extremely large, in keeping with the strong electrostatic attraction associated with ionic binding. The interaction energies of the BF_3·ONF complexes (**13**) and (**15**) are noticeably larger than those of BF_3·ONF (**14**) and BF_3·ONCl (**16**). This is because in (**13**) and (**15**) there are four separate interaction sites between the N and O atoms and the out-of-plane F atoms, which reinforce one another, and in (**16**) there are three, one Cl···O and two N···F attractive connections, while in (**14**) the only interaction is a single F···N bond (see Fig. 3).

The perturbations of the internal bond lengths of the interacting monomers are collected in Table 2. For the neutral ONCl complexes (**11**) and (**12**), the BF bond lying in the symmetry plane is slightly elongated, while those straddling the plane contract by a small amount. The NO bonds are hardly affected by the interaction, but the NCl bond in the Cl-bound complex is substantially stretched as a result of the association, but is shortened in the N-bound complex to compensate partly for the loss of electron density around the nitrogen atom due to the donation to the boron atom. The situation is much more dramatic for the ion-pair complexes, where all the BF bonds are lengthened considerably relative to those in BF_4^- and $BClF_3^-$, particularly the out-of-plane BF bonds in (**13**), (**15**) and (**16**). The NO bond lengths contract by a relatively constant amount with respect to NO^+, due to the loss of antibonding
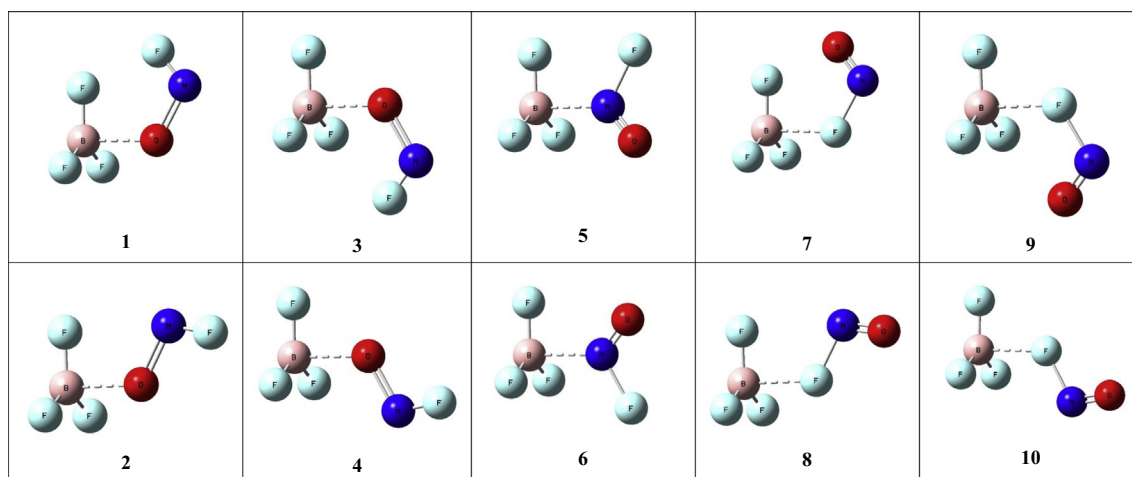

Fig. 1. Starting structures for the geometry optimizations of the BF_3·ONF complexes.