Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Structure 834–836 (2007) 30–41

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

The vibrational spectra of the boron halides and their molecular complexes. Part 9. *Ab initio* studies of the complexes of boron trifluoride with methanol, methanethiol and some related bases

Thomas A. Ford *

Centre for Theoretical and Computational Chemistry, School of Chemistry, University of KwaZulu-Natal, Durban 4041, South Africa

Received 25 July 2006; accepted 29 September 2006
Available online 24 January 2007

Abstract

The structures, interaction energies and vibrational spectra of the electron donor-acceptor complexes formed between boron trifluoride, as Lewis acid, and methanol and methanethiol, as Lewis bases, have been determined by means of *ab initio* calculations at the level of second order Møller–Plesset perturbation theory, using a triple-zeta Gaussian basis set with polarization and diffuse functions on all atoms. Two conformers, an eclipsed and a staggered species, have been examined for each complex, and the preferred conformer identified in each case. The computed data have been compared with those for some related complexes containing boron trifluoride and other oxygen and sulphur electron donors (water, hydrogen sulphide, dimethyl ether and dimethyl sulphide).

Keywords: *Ab initio* calculations; Molecular complexes; Boron trifluoride; Methanol; Methanethiol; Molecular structures; Interaction energies; Vibrational spectra

1. Introduction

The vibrational spectra and related properties of the electron donor–acceptor complexes of boron trifluoride with water and hydrogen sulphide have recently been reported [1], at the level of second order Møller–Plesset perturbation theory (MP2) [2], employing a variety of basis sets. These basis sets consist of double- and triple-zeta bases, with various combinations of polarization and diffuse functions on the heavy atoms only, and on all atoms [3–10]. The most extensive basis set used, 6-311++G(d,p) [9,10], was found to yield the most consistent set of data, measured by the highest level of agreement between the computed geometrical parameters and vibrational spectra of the monomer species with the experimental values reported in the literature. We have also reported similar calculations on the corresponding complexes of boron trifluoride with dimethyl ether and dimethyl sulphide [11,12], at the restricted Hartree–Fock (RHF) level, and using density functional theory (DFT) with the B3LYP functional [13–15], with the 6-31G(d,p) basis set [3–7]. In addition, we have recorded the infrared spectra of the $BF_3 \cdot H_2O$ [16], $BF_3 \cdot (CH_3)_2O$ and $BF_3 \cdot (CH_3)_2S$ [12] complexes in nitrogen and argon matrices. In this work, we have extended the range of oxygen and sulphur bases to include methanol and methanethiol, in order to examine the effects of successive methyl substitution on the computed properties of the complexes. We have carried out the calculations using MP2/6-311++G(d,p) methodology [2,9,10], for consistency with our results for $BF_3 \cdot H_2O$ and $BF_3 \cdot H_2S$ [1], and for valid comparison among the different families of complexes we have upgraded the computations on $BF_3 \cdot (CH_3)_2O$ and $BF_3 \cdot (CH_3)_2S$ to the same level of theory and the same basis set.

Although a substantial amount of work has been carried out on the complexes of BF_3 with H_2O, H_2S, $(CH_3)_2O$ and $(CH_3)_2S$, which has been cited in our

---

* Tel.: +27 31 260 1096; fax: +27 31 260 3091.
E-mail address: ford@ukzn.ac.za

0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.09.039

earlier publications [1,11,12,16], only two reports of the properties of the $BF_3{\cdot}CH_3OH$ complex have appeared [17,18], and none on $BF_3{\cdot}CH_3SH$. In these studies, electron energy loss (EELS) and ultraviolet photoelectron spectroscopies (UPS) were employed to determine the orbital energies of the interacting monomers and of the complex, and the transition energies among them. These studies extended similar investigations of the $BF_3{\cdot}H_2O$ [17–19] and $BF_3{\cdot}H_2S$ [17,18,20] complexes, in which it was shown that the shifts in the energies of the fluorine lone pair orbitals, and of the transitions associated with them, are proportional to the strength of the donor–acceptor interaction.

In this publication, we present the results of our calculations of some properties of the $BF_3{\cdot}CH_3OH$ and $BF_3{\cdot}CH_3SH$ adducts, and relate them to comparable studies on the analogous complexes of BF_3 with H_2O, H_2S, $(CH_3)_2O$ and $(CH_3)_2S$, and we examine the effect of successive methyl substitution on such properties in the two families of associated species.

2. Computational details

The calculations were carried out using the Gaussian-98 computer program [21], at the level of second order Møller–Plesset perturbation theory [2] with the

Table 1
Percentage calculated – experimental errors, and root mean square errors, of the geometrical parameters of the monomers

Monomer	Parameter[a]	Percentage error	RMS error	Monomer	Parameter[a]	Percentage error	RMS error
BF_3	r(BF)	0.87	0.87				
H_2O	r(OH)	0.11	0.66	H_2S	r(SH)	−0.16	0.12
	HOH	−0.93			HSH	−0.03	
CH_3OH	$r(CH_{ip})$	−0.81	1.94	CH_3SH	$r(CH_{ip})$	−0.11	0.63
	$r(CH_{op})$	−0.19			$r(CH_{op})$	−0.17	
	r(CO)	−0.50			r(CS)	−0.77	
	r(OH)	−1.60			r(SH)	−0.61	
	$H_{ip}CH_{op}$	−0.52			$H_{ip}CH_{op}$	0.13	
	$H_{op}CH_{op}$	−0.06			$H_{op}CH_{op}$	−1.30	
	COH	−0.24			CSH	−0.29	
$(CH_3)_2O$	$r(CH_{ip})$	−2.46	1.29	$(CH_3)_2S$	$r(CH_{ip})$	−2.17	1.33
	$r(CH_{op})$	−1.67			$r(CH_{op})$	−2.06	
	r(CO)	−0.28			r(CS)	−0.24	
	$H_{ip}CH_{op}$	−0.03			$H_{ip}CH_{op}$	−0.74	
	$H_{op}CH_{op}$	−0.52			$H_{op}CH_{op}$	0.37	
	COC	−0.91			CSC	−0.94	

[a] H_{ip} and H_{op} and the hydrogen atoms in the symmetry plane and out of the symmetry plane respectively.

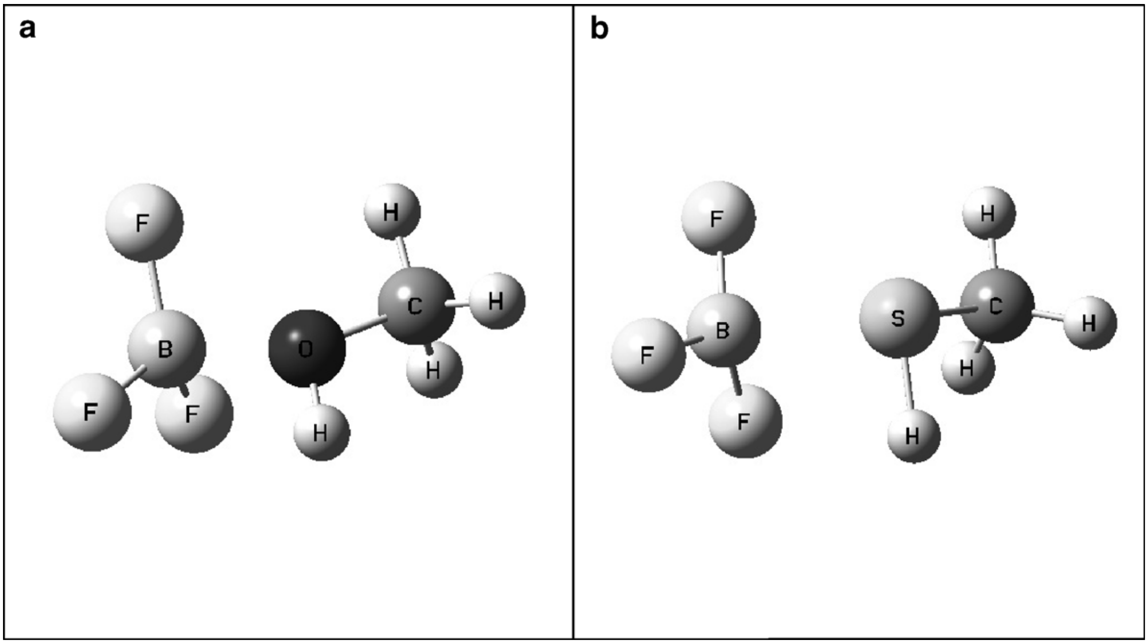

Fig. 1. Optimized structures of the (a) $BF_3{\cdot}CH_3OH$ and (b) $BF_3{\cdot}CH_3SH$ complexes.