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Ab initio studies of the properties of some halogen-bonded complexes of ammonia, water, phosphine and hydrogen sulphide

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ABSTRACT

Ab initio calculations, at the second order level of Møller–Plesset perturbation theory and with Dunning's augmented correlation-consistent polarised valence triple-zeta basis set, have been carried out on two series of molecular complexes. One set consists of the common bases ammonia, water, phosphine and hydrogen sulphide and the electron-acceptor halogens difluorine, dichlorine and dibromine, and the other comprises the interhalogens bromine fluoride, chlorine fluoride and bromine chloride as electron acceptors, with the same set of four bases. The interaction energies, molecular structures, vibrational spectra and charge distribution properties of the complexes have been computed, and the adducts have been characterised as halogen-bonded complexes. The trends in the values of these properties correlate with systematic changes in the base and the halogen species. The computed physical data are in quite good agreement with such experimental results as are available, while the anomalous features of some of the properties of the complexes with phosphine have been rationalised.

1. Introduction

The term "halogen bond" was apparently coined by Dumas et al. in 1978 in a report of the detection of the electron donor–acceptor complexes formed between carbon tetrachloride and tetrabromide and some oxygen and nitrogen bases, in which the halogen atom interacted directly with the oxygen or nitrogen atom [1]. Many other reports have since appeared of the observation of similar complex species, including some containing NH_3 [2–11], H_2O [11–17], PH_3 [4,5,11,18,19] and H_2S [4,8,10,11,20–23] as electron donors, of relevance to the present work. These complexes are known generically as halogen-bonded complexes, and the properties of these unusual non-covalent adducts have been extensively reviewed [10,24–27]. The source of the interaction is interpreted in terms of electrostatic potentials. The lone pairs of electrons on atoms such as N, O, P and S represent sites of high electron density, and the peripheral surface of a halogen-containing molecule at the halogen "end" of the molecule is a region of positive electrostatic potential, the so-called σ-hole [24–27]. The attraction of these electropositive and electronegative regions confers some stability on the adduct and, since the positive electrostatic potential acts along the direction of the σ bond to the halogen atom, this leads to a high degree of directionality in the halogen bond. This feature draws attention to the fundamental similarity between the halogen bond and the hydrogen bond (in which, in the complex $ClH{\cdot}NH_3$, for example, the region of positive electrostatic potential of HCl, located at the hydrogen atom "end" of the HCl molecule, interacts collinearly with the lone pair associated with the nitrogen atom of NH_3). Thus we would expect the complexes formed between NH_3, H_2O, PH_3 and H_2S as electron donors and halogen or interhalogen molecules as electron acceptors to have a range of properties in common with the analogous hydrogen-bonded complexes of acids such as HF, HCl and HBr with the same set of bases. In this paper we explore a series of such halogen-bonded complexes with a view to establishing whether those properties governed by the natures of the electron donor and acceptor, namely interaction energies, molecular geometries, vibrational spectra and charge transfer, show the same trends as those of some corresponding simple hydrogen-bonded complexes as the acid and base molecules are varied systematically.

The microwave spectroscopic work of Legon and co-workers [2–23] has built up an extensive library of physical data, including rotational constants, centrifugal distortion constants and nuclear quadrupole coupling constants, on those intermolecular complexes formed between the bases listed above and the halogen (F_2, Cl_2 and Br_2) and interhalogen (BrF, ClF and BrCl) molecules with which to compare the results of our computational studies. Thus we were able to initiate this project with a good understanding of the trends in the complex properties to be expected. *Ab initio* studies of some of the complexes which make up the subject of the present investigation have also appeared [14–17,23,28–33], so there are also some theoretical data against which our results may be measured.

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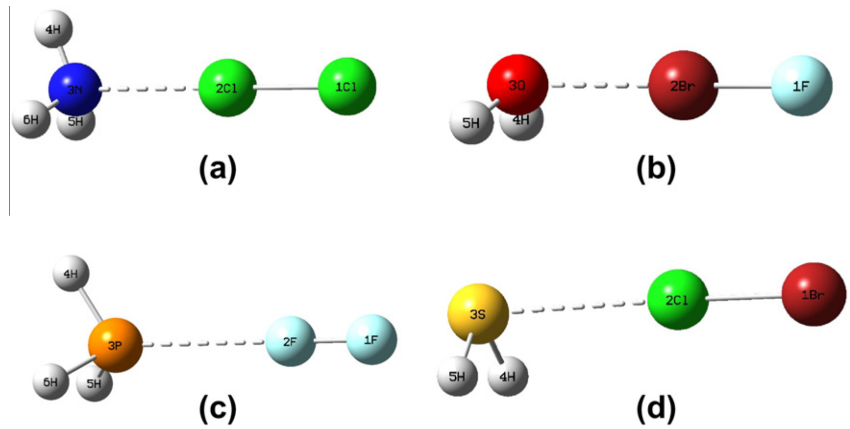

Fig. 1. Optimised structures of (a) $NH_3{\cdot}Cl_2$; (b) $H_2O{\cdot}BrF$; (c) $PH_3{\cdot}F_2$; (d) $H_2S{\cdot}ClBr$.

Table 1
Interaction energies of the halogen-bonded complexes of NH_3, H_2O, PH_3 and H_2S with F_2, Cl_2, Br_2, BrCl, ClF and BrF. Numbers in parentheses are literature *ab initio* results.

Electron acceptor	Interaction energy (kJ mol^{-1})			
	NH_3	H_2O	PH_3	H_2S
F_2	−5.34 (−7.24[a])	−3.66 (−5.3[b])	−3.29	−2.51
Cl_2	−17.54 (−10.38[c], −17.2[d], −25.40[e])	−8.91 (−11.8[f])	−11.06	−8.81
Br_2	−25.82	−11.76	−20.25	−13.24
BrCl (Cl-bound)	−13.11	–[g]	−8.85	−7.43
BrCl (Br-bound)	−32.54 (−50.84[h])	−14.17 (−18.6[i], −20.92[j])	−31.77	−16.06 (−22.68[h])
ClF (Cl-bound)	−44.79 (−27.07[c], −38.9[d], −49.16[e], −69.33[h])	−16.33 (−20.33[j], −21.2[b], −27.91[h])	−91.31	−19.67 (−34.27[h])
BrF (Br-bound)	−58.68 (−78.95[h])	−23.98 (−36.40[h])	−75.23	−30.66 (−41.13[h])

[a] Ref. [32].
[b] Ref. [14].
[c] Ref. [28].
[d] Ref. [29].
[e] Ref. [31].
[f] Ref. [15].
[g] Converged as a saddle point.
[h] Ref. [33].
[i] Ref. [16].
[j] Ref. [30].

2. Computational details

The calculations were performed using the Gaussian-09 package [34], at the second order level of Møller–Plesset perturbation theory (MP2) [35], and employing Dunning's augmented correlation-consistent polarised valence triple-zeta basis set (aug-cc-pVTZ) [36–40]. Geometry optimizations were carried out with all parameters allowed to vary freely, subject to the imposition of C_{3v} symmetry for the complexes with NH_3 and PH_3, and C_s symmetry for the H_2O and H_2S species. The interaction energies were computed, and corrected for basis set superposition error (BSSE) [41] by the full counterpoise method [42], and for zero-point energy differences. The vibrational analyses were carried out in the anharmonic approximation. Natural bond orbital (NBO) analyses [43] were applied, in order to provide information on the electron redistributions occurring on complexation, and to identify which orbitals of the electron donors and acceptors were chiefly involved in the interactions.

3. Results and discussion

All the complexes converged with qualitatively similar structures, with the halogen and interhalogen molecules interacting with the axes of the lone pair orbitals of the electron donor molecules in a virtually linear fashion (for the NH_3 and PH_3 complexes the axes of the halogen or interhalogen molecules were fixed to be collinear with the C_3 axes of the bases; this constraint was considered justified in the light of the experimental observation that all the complexes with NH_3 and PH_3 were found to be symmetric tops [2–11,18,19]). For the adducts with H_2O and H_2S these angles deviated from linearity by no more than 2°, and this observation is also consistent with the experimental evidence [4,8,10,11–17,20–23]. The complexes with F_2, Cl_2 and Br_2 all optimised as genuine minima. Those with the interhalogens bound through the more electropositive halogen atom were also all genuine minima, consistent with the finding that no "reverse-bound" complexes bound through the more electronegative halogen atom were observed experimentally [2,5,8,9–11,13,14,16,21]. The reverse-bound species were all saddle points, with the exceptions of the Cl-bound adducts of BrCl with NH_3, PH_3 and H_2S, which also yielded a full set of real vibrational modes. This is because BrCl, being the least polar interhalogen molecule, does not present a large difference in the properties of the interacting atom, Br or Cl, to the electron donor atom, and the resulting complexes are all stable species. The structures of a sample of the complexes are illustrated in Fig. 1.

The interaction energies of the two families of complexes are presented in Table 1. In general, the interhalogen complexes are significantly more strongly bound than the halogen set. The strengths of interaction increase systematically in each series with the gas phase basicity of the base [44] and with the polarisability of the halogen [45]. These relationships are shown in Figs. 2 and 3. It appears from Fig. 2b that the interaction energies of the complexes