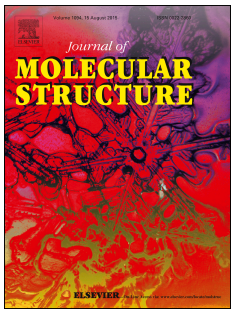
Accepted Manuscript



Towards a better understanding of the parameters determining the competition between bromine halogen bonding and hydrogen bonding: An FTIR spectroscopic study of the complexes between bromodifluoromethane and trimethylamine

Yannick Geboes, Frank De Proft, Wouter A. Herrebout

PII: S0022-2860(18)30420-4

DOI: 10.1016/j.molstruc.2018.03.123

Reference: MOLSTR 25062

To appear in: *Journal of Molecular Structure*

Received Date: 6 November 2017

Revised Date: 20 March 2018

Accepted Date: 27 March 2018

Please cite this article as: Y. Geboes, F. De Proft, W.A. Herrebout, Towards a better understanding of the parameters determining the competition between bromine halogen bonding and hydrogen bonding: An FTIR spectroscopic study of the complexes between bromodifluoromethane and trimethylamine, *Journal of Molecular Structure* (2018), doi: 10.1016/j.molstruc.2018.03.123.

Towards a better understanding of the parameters determining the competition between bromine halogen bonding and hydrogen bonding: an FTIR spectroscopic study of the complexes between bromodifluoromethane and trimethylamine.

Yannick Geboes[a,b], Frank De Proft[b] and Wouter A. Herrebout[a]*

[a] *Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp (Belgium), E-mail: Wouter.herrebout@uantwerpen.be*

[b] *Eenheid Algemene Chemie (ALGC), Member of the QCMM VUB-UGent Alliance Research Group, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels (Belgium)*

Corresponding Author:

W.A. Herrebout: e-mail: wouter.herrebout@uantwerpen.be, +32/3.265.33.73

Keywords: noncovalent interactions, halogen bonding, hydrogen bonding, FTIR, cryospectroscopy

Abstract

Previous experimental and theoretical studies of various model compounds dissolved in liquid noble gases have shown that iodine halogen bonding can compete with hydrogen bonding and that experimental information on the thermodynamic equilibria present can be derived. To get a more general grasp of the competition between halogen bonding and hydrogen bonding, and to expand the set of experimental data to other, weaker, halogen donors, solutions in liquid krypton containing mixtures of bromodifluoromethane with trimethylamine or the fully deuterated trimethylamine-d_9 are studied using FTIR spectroscopy. Analysis of the experimental data obtained is supported by *ab initio* calculations, statistical thermodynamics and Monte Carlo-Free Energy Perturbation calculations. Careful comparison of the spectra of the monomers and of the mixtures studied, shows that for all solutions studied, only features due to a hydrogen-bonded complex are observed. The experimental complexation enthalpy for this species is determined to be -14.2(4) kJ mol^{-1}.