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with the dihalogens Br<sub>2</sub> and I<sub>2</sub>**

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# Computational characterization of the charge transfer (CT) and T-shaped molecular complexes of N-methyl imidazoline-2-thione and N-methyl imidazolidine-2-thione with the dihalogens Br<sub>2</sub> and I<sub>2</sub>

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## Abstract

The computational characterization of the molecular complexes of N-methyl imidazoline-2-thione (methimazole) and the related saturated analog, N-methyl imidazolidine-2-thione with Br<sub>2</sub> and I<sub>2</sub> is carried out using quantum mechanical electronic structure methods. Two kinds of molecular connectivity have been examined. The first displays a collinear S-X-X geometry (X=Br, I) and leads to charge-transfer type (CT) adducts, possible in two stereoisomeric conformations depending on the direction of the X<sub>2</sub> axis, either planar or perpendicular to the NCS plane. The second kind corresponds to T-shaped hypervalent complexes in which sulfur is connected to both X atoms forming the linear X-S-X arrangement. The structural changes, the spectroscopic findings, the NBO analysis and the examination of the MO second order perturbation energies give interesting information about the nature of the halogen bonding interaction between the electron donor organic species and the electron acceptor dihalogen molecule. Similar trends are followed by the energy and relative stability results including BSSE corrections, which show the larger stabilization of the planar CT conformers of both dihalogens vs. the perpendicular configurations. They also indicate the higher stability of the T-shaped bromine complexes relative to the CT species, opposite to the energy order of the corresponding diiodine adducts. A critical comparison is carried out with literature results on similar systems.

**Keywords :** Halogen bonding ; Charge transfer ; Hypervalent complexes

## 1. Introduction

Among the non-covalent interactions, there is a second interesting exception in addition to the hydrogen bonding case : the case of halogen bonding [1-3] which, like hydrogen bonding, is also characterized by intermolecular distances shorter than the range of van der Waals distances. As it has been recently reviewed [1-3], the tendency of diiodine to form complexes with Lewis bases has been repeatedly recognized since at least the middle of the nineteenth century. Eventually, with the development of X-ray crystallography and modern spectroscopic techniques, the directionality and strength of this type of halogen bonds have been investigated in great detail [1-3]. In his analytic report, Karpfen [1] describes the way in which the term *halogen bonding* has been eventually introduced for any complexes of the dihalogens  $X_2$ ,  $XY$  ( $X, Y =$  halogen atoms) with different Lewis bases as interaction partners. Originally, complexes of this type were characterized as charge-transfer (CT) or electron donor-acceptor complexes [1]. Later, the above more general definition of halogen bonding complexes has been adopted, following closely the analogy to hydrogen bonding cases. It was thus, suggested [1-3], that any non-covalent intermolecular arrangement  $A-X\cdots B$  where  $X$  is a halogen atom and  $B$  an electron donor, represents a halogen bonding species which may be included in the current definition [2]. The resulting charge-transfer complex may be classified as a halogen bonded adduct showing the typical characteristics of this interaction, namely the elongation of the  $A-X$  equilibrium distance and the red-shifting of the  $A-X$  stretching frequency [2].

As said, halogen bonding is widely recognized nowadays as the most important non-covalent interaction after hydrogen bonding [1-3]. It is largely an electrostatic phenomenon and the most electronegative the element to which the

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3 halogen is bound to, for example O or N, the better electron acceptor becomes.  
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5 Fluorine has proved to be a poor electron acceptor, forming very weak halogen  
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7 bonds, if at all. In the numerous investigations, several series of simple molecules  
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9 have been studied as Lewis bases B, among them CO, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O, H<sub>2</sub>S HCN,  
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11 NH<sub>3</sub>, N(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>CN, H<sub>2</sub>CO, PH<sub>3</sub>, benzene derivatives, furan, thiophene and  
12  
13 saturated rings like oxirane and thiirane [1-3]. Current interest into halogen bonded  
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15 complexes has expanded to include organohalogen and inorganic halide acceptors  
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17 [1-7]. However, the dihalogens (X<sub>2</sub>) and interhalogens (XY) continue to attract  
18  
19 attention and the study of diiodine complexes with organic frameworks involving  
20  
21 sulfur and selenium electron donors still receives intensive consideration because of  
22  
23 the variety of the potential biological, pharmaceutical and electronic material  
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25 applications of these complexes [8-19]. As pointed out by Pennington et al. [3],  
26  
27 “among the many applications involving X<sub>2</sub> and XY halogen bonding, this type of  
28  
29 interaction is increasingly being discovered to play a significant role in biochemical  
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31 systems, particularly in thyroid chemistry”. While halogen bonding involving the  
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33 halogenated thyroid enzymes is often the focus of studies in this area, the role of I<sub>2</sub> is  
34  
35 also of interest since it is closely related to numerous investigations into the  
36  
37 interaction of antithyroid drugs with I<sub>2</sub> [3]. Indeed, a prominent member among the  
38  
39 group of sulfur electron-donor compounds is N-methyl imidazoline-2-thione,  
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41 commercially available as methimazole, which has been widely used in the treatment  
42  
43 of hyperthyroidism. Its diverse properties have been attributed to the high  
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45 coordination ability of the RN-C(=S)-NR’ heterocyclic thioamide group to both  
46  
47 metallic and non-metallic elements, leading to stable electron donor-acceptor  
48  
49 complexes. The crystallographic and theoretical studies have established two kinds of  
50  
51 connectivity for the dihalogen complexes of methimazole and related organic  
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53 frameworks. The first corresponds to charge transfer type (CT) adducts containing the  
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3 linear S-X-X geometry and possible in two stereoisomeric conformations with the  
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5 X<sub>2</sub> molecular axis being either planar or perpendicular with respect to the NCS  
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7 plane. The second type corresponds to the T-shaped hypervalent complexes in which  
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9 sulfur is connected to both X atoms forming the linear X-S-X arrangement.  
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13 In the present work a detailed computational study is carried out on the  
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15 structural and energy characteristics of the CT and T-shaped molecular complexes of  
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17 N-methyl imidazoline-2-thione (denoted hereafter as M) and the related saturated  
18  
19 analog N-methyl imidazolidine-2-thione (denoted as M') with Br<sub>2</sub> and I<sub>2</sub>. The  
20  
21 comparison between the various conformeric isomers and the bromine and iodine  
22  
23 complexes shows interesting effects on the stabilization of the particular type of  
24  
25 connectivity, that may be attributed at a first glance to the different electronegativity  
26  
27 and other factors such as a secondary hydrogen bonding interaction. However,  
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29 natural bond orbital (NBO) calculations are performed in order to get a deeper insight  
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31 into the nature of the bonding and the strength of the intermolecular interactions and  
32  
33 obtain in this way a good evaluation of the delocalization effects. Despite several  
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35 interesting investigations on methimazole derivatives already reported [17], we  
36  
37 believe that the present work presents many differences with previous studies and  
38  
39 several new features are examined. For example, in contrast to previous reports  
40  
41 where both nitrogen atoms of the methimazole ring bear each, a methyl group [17],  
42  
43 our system contains one nitrogen atom bound to a methyl group and the other  
44  
45 connected to a H atom. Thus, the present model system allows the additional  
46  
47 investigation of a possible secondary hydrogen-halogen interaction not available in  
48  
49 other reported cases [17]. Our study also extends to the saturated analog and it  
50  
51 allows a comparison of the strength of the charge-transfer interaction in both the  
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53 imidazoline and imidazolidine organic frameworks, that is not reported previously.  
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60 There are differences in the methodologies too, which will be analysed in the

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3 Computational details section. We would just like to mention here only the BSSE  
4 energy corrections which have been performed in the present work and which are  
5 considered to be very important for the proper evaluation of the energy results in  
6 non-covalent interacting systems. Therefore, we believe that there are many new  
7 points considered in the present study and the detailed comparison with other  
8 reported computational results on methimazole derivatives and similar systems  
9 would present a lot of interest.  
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## 22 **2. Computational details**

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24 While the general features of halogen bonding are by now well established, it is  
25 becoming a challenge to predict the molecular parameters of halogen bonded  
26 complexes and verify the experimentally observed trends using high-level quantum  
27 mechanical computational techniques. The basic issue in these studies is the search  
28 of reliable computational techniques and appropriate basis sets to describe such  
29 systems as best as possible taking into account the large size of them and the  
30 corresponding computational cost.  
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41 The electronic molecular structure calculations have been performed using the  
42 Gaussian 98 series of programs [20]. The restricted second-order Møller-Plesset  
43 (MP2) level of theory has been employed in combination with different basis sets for  
44 the various atoms involved. The halogens have been treated using the orbital-  
45 adjusted ECP plus DZ effective core potential method of Hay and Wadt, i.e., the  
46 LANL2DZ basis set [21]. It is worth noting here the need, often stressed in the  
47 literature, for the use of additional polarization functions in combination with the  
48 valence LANL2DZ basis set in order to achieve a more accurate description of the  
49 halogen atom in halogen bonded charge-transfer complexes [22, 23]. Thus,  
50 additional polarization functions have been employed to increase the halogen  
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3 valence basis sets in order to describe as best as possible the polarization of the  
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5 halogen atoms [24]. Specifically, the Br valence basis set was augmented with two *d*  
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7 and one *f* polarization functions from the cc-pvTZ basis set [25]. For the iodine  
8  
9 treatment two *d* and one *f* polarization functions were taken from the Stuttgart-Bonn  
10  
11 ECPnMDF (Dirac-Fock) relativistic potential [26]. We believe that the enlargement  
12  
13 of the halogen valence-bond LANL2DZ basis set with additional polarization  
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15 functions consists a significant improvement over previously reported calculations  
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17 on similar methimazole systems. The 6-31G+(d) basis set was used for sulfur in order  
18  
19 to account for a possible diffusion of its valence functions due to the non-covalent  
20  
21 halogen bonding interaction and the 6-31G(d,p) one for the other atoms.  
22  
23 Considering the large size of the molecules under investigation and the large number  
24  
25 of atoms involved, the level of theory employed in the present study should be  
26  
27 satisfactory and comparable or even higher than the levels of theory employed in the  
28  
29 study of similar systems by other workers.  
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36 As described in the Introduction section, the present work aims at investigating  
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38 molecular interaction energies of relatively weakly bonded gas-phase systems. For  
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40 such systems the consideration of the limited basis set effects is a necessary  
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42 requirement arising from the superposition of these finite basis sets in the  
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44 optimization procedure, due to the different number of basis functions considered in  
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46 the complex and the monomers optimizations. Thus, the basis set superposition error  
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48 (BSSE) correction is an important issue in the proper treatment of non-covalent  
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50 intermolecular interactions and it has been shown to be sizably large for a series of  
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52 of relevant species [10]. Hence, BSSE calculations following the functional  
53  
54 counterpoise scheme [27], have been additionally carried out for the present  
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56 molecular complexes, in order to amend properly the computed binding energies  
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58 and relative stabilities. This is another difference with several reported calculations  
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3 on methimazole related systems [17] that, in our opinion, give additional merit to  
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5 the present results.  
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### 10 **3. Structural and spectroscopic results**

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12 Tables 1 and 2 contain the calculated structural and spectroscopic results and  
13  
14 compare with literature data. Fig. 1 displays the optimized structures of the adducts  
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16 between the organic donors and the dihalogens only for the case X= Br, since the  
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18 iodine complexes present similar geometries. The results are in good agreement with  
19  
20 the reported experimental evidence and previous theoretical calculations and the  
21  
22 comparison with DFT calculations (Table 1) reconfirms the tendency of the MP2  
23  
24 methodology to predict tighter structures than the density functional theory techniques  
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26 [17]. Two types of stereoisomeric charge-transfer (CT) complexes have been obtained  
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28 between N-methyl imidazoline-2-thione, denoted as M and the related saturated  
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30 analog N-methyl imidazolidine-2-thione, denoted as M' and the dihalogens. Both  
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32 configurations feature a collinear S-X-X geometry. In the first type, the torsional  
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34 angle NCSX (where N is the amidic N-H nitrogen atom) around the C=S bond is  
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36 close to 0° for the M-XX species or a little disturbed in the range 14-18° for the case  
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38 of the M'-XX complexes, indicating that the dihalogen molecular axis is slightly  
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40 displaced off the thioamide plane. The second type presents a perpendicular  
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42 arrangement of the dihalogen molecular axis with respect to the thioamide plane and  
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44 exhibits a NCSX torsional angle ranging from 96° to 99°. The corresponding  
45  
46 geometries are denoted hereafter as planar and perpendicular, respectively. The T-  
47  
48 shaped hypervalent isomers present a near perpendicular arrangement of the X-S-X  
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50 line relative to the thioamide plane.  
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The three isomeric species of each family show several interesting geometrical features which may be correlated to a certain extent with the NBO



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3 occupation numbers and the energy stabilization tendencies. The main important  
4 structural variation is the significant elongation of the C-S bond distance of the order  
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6 of 0.25 Å in both conformations of iodine and bromine CT complexes compared to  
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8 the free M, M' species. This elongation becomes even more pronounced in the case  
9  
10 of the T-shaped hypervalent adducts where the C-S bond distance increases by  
11  
12 about 0.5- 0.8 Å compared the free organic frameworks. Another interesting change  
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14 is the significant expansion of the X-X bond in the CT adducts, particularly in the  
15  
16 planar complexes. The S-X distance also shows important variations and decreases in  
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18 the planar configurations relative to the perpendicular structures, reducing further in  
19  
20 the T-shaped complexes. Specifically, the S-X length decreases by 0.110 Å from  
21  
22 M-II (planar) to MI<sub>2</sub> (T-sh), 0.156 Å from M'-II (planar) to M'I<sub>2</sub> (T-sh), 0.144 Å  
23  
24 from M-BrBr (planar) to MBr<sub>2</sub> (T-sh) and 0.199 Å from M'-BrBr (planar) to  
25  
26 M'Br<sub>2</sub> (T-sh). The saturated imidazolidine T-shaped complexes with both  
27  
28 dihalogens slightly differentiate the two S-X distances leading to smaller S-X  
29  
30 values for the X closer to the methylic N. It is interesting to mention here that  
31  
32 the calculated S-Br distances obtained in the T-shaped complexes approach S-Br  
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34 bound distances (similar for example with those of species like BrSSBr [28]),  
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36 faster than the corresponding S-I bond lengths, with relevant consequences in the  
37  
38 stabilization of the corresponding adducts. Indeed, the larger reduction of the S-X  
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40 distance in the bromine T-shaped hypervalent complexes, i.e., 0.144 Å and 0.199 Å  
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42 for the bromine M and M' complexes relative to 0.110 Å and 0.156 Å for the  
43  
44 iodine M and M' adducts respectively, may be correlated with the higher  
45  
46 electronegativity of bromine and may be the explanation for the larger stabilization  
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48 of the T-shaped adducts vs the CT structures in the bromine family. This observation  
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50 is supported by the examination of the NBO occupation numbers, we shall see at the  
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52 next section.  
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4 The N-H bond distance shows a mild increase upon complexation, particularly  
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6 in the planar CT type geometries, reflecting a possible additional interaction of the  
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8 amidic hydrogen with the inner halogen atom, favoured mainly in the coplanar  
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10 configurations. This secondary intramolecular hydrogen bonding interaction has also  
11  
12 been observed in a large number of related systems [10] and it is much better  
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14 demonstrated in the N-H stretching frequency shift that takes place upon  
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16 complexation, resulting in the higher stabilization of the planar configurations *vs*  
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18 the perpendicular arrangement, as we shall see next. The angular parameters show  
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20 less pronounced differentiations between the planar and the perpendicular structures  
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22 and the T-shaped isomers. We only note that the planar M'-XX configurations  
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24 involve a small but non-negligible deviation from the planar geometry, 18.1° for  
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26 M'-II and 15.5° for M'-BrBr planar CT complexes.

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32 The main spectroscopic feature that emerges from the harmonic vibrational  
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34 frequency analysis, is the shift in the NH stretching frequency observed in the IR  
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36 spectra of the adducts compared to the free organic species (Table 2). This frequency  
37  
38 shifting may be related to the slight extension of the amidic N-H bond in the planar  
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40 M-XX, M'-XX complexes, discussed above, and implies the possible operation of an  
41  
42 additional intramolecular NH...X hydrogen bonding interaction that contributes to  
43  
44 the stabilization of the planar complexes. Thus, the inner I atom and to a much lesser  
45  
46 extent the inner Br atom, may be considered to show an amphoteric behavior in the  
47  
48 planar complexes acting additionally to a small extent as an electron donor to the  
49  
50 acidic H of the amidic NH group and affecting the vibrational harmonic frequency.  
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52 The calculated unscaled harmonic frequency shift  $\Delta\nu(\text{NH}) = 103.7 \text{ cm}^{-1}$  for the M-II  
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54 (planar) complex reproduces fairly close the experimental value, 90  $\text{cm}^{-1}$  [8], much  
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56 closer than other computational studies [13] (Table 2), confirming the reliability of  
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3 the level of theory employed in the present work. Good consistency is also observed  
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5 between the  $\Delta\nu(\text{NH})$  values of the M'-II complexes calculated in the present work,  
6  
7  $\sim 60 \text{ cm}^{-1}$ , and the experimental results ranging from 52 to 61  $\text{cm}^{-1}$  for the diiodine  
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9 CT complexes of a series of compounds belonging to the imidazolidine family [29].  
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#### 12 13 14 15 **4. NBO analysis and energy-relative stability results**

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17 The NBO occupation numbers for the charge-transfer M-II, M'-II and M-BrBr (both  
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19 conformers) and the hypervalent  $\text{MX}_2$ ,  $\text{M}'\text{X}_2$  (X=I, Br) T-shaped complexes, are  
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21 summarized in Tables 3 and 4. Table 5 displays the second-order perturbation  
22  
23 energies  $E^{(2)}$  corresponding to the main charge-transfer interactions present.  
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27 The analysis of these data is in good agreement with the structural trends and  
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29 the frequency shift calculations and gives interesting information about the nature and  
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31 the strength of the halogen bonding. For instance, the occupation number of the  $\sigma_1(\text{C}-$   
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33 S) bonding orbital decreases in all cases upon complexation, reflecting the reduction  
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35 of electron density due to the partial transfer to the  $\text{S}\cdots\text{X}$  (X=I, Br) interaction.  
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37 Comparison of the planar and perpendicular geometries is revealing too. The  $\sigma^*(\text{N}-\text{H})$   
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39 antibonding orbital occupation number increases upon complexation from 0.0114  
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41 in free M to 0.0116 in M-II (perp) and 0.0235 in M-II (plan) with similar results  
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43 for the M'-II and M-BrBr complexes. The increase is most pronounced in the planar  
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45 configurations and is an additional evidence for a possible, secondary interaction of  
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47 the hydrogen bonding type between the amidic hydrogen and the halogen atom,  
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49 favoured in the planar geometry. It is readily manifested in the larger stabilization  
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51 of the planar conformers, as we shall see in the next paragraph. On the other hand,  
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53 the smaller increase of the  $\sigma^*(\text{N}-\text{H})$  antibonding orbital occupation number in the M-  
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55 BrBr (plan), i.e., from 0.0114 to 0.0220, vs the iodine planar complexes is a clear  
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57 indication of the poorer capacity of bromine compared to iodine, to play an  
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3 amphoteric role, i.e., to act primarily as an electron acceptor for sulfur and  
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5 secondarily as an electron donor for the amidic hydrogen due to its higher  
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7 electronegativity. This feature is reflected too in the lower  $\Delta H_r^{298}$  value of M-BrBr  
8  
9 (plan). Another relevant characteristic is the larger  $\sigma^*(X-X)$  antibond occupation  
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11 number in the coplanar arrangement vs the perpendicular, which can be rationalized  
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13 in terms of the charge transfer interactions between orbitals. As shown in Table 5,  
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15 the S lone pair,  $LP_3(S)$ , participate as donor and the  $\sigma^*(X-X)$  antibond as acceptor in  
16  
17 a strong intermolecular charge transfer interaction  $LP_3(S) \rightarrow \sigma^*(X-X)$  for which the  
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19 corresponding energies  $E^{(2)}$  for M-II (plan) and MBrBr (plan) (64.37 and 73.97 kcal  
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21  $mol^{-1}$  respectively) are much larger than for MII (perp) and MBrBr (perp) (53.17  
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23 and 56.77 kcal  $mol^{-1}$ ). Of interest is also the larger occupation number  $LP_3(S)$  in  
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25 both planar iodine and bromine charge-transfer complexes vs the perpendicular  
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27 conformers and the non-negligible charge transfer energy  $E^{(2)}$  for  $LP_3(X) \rightarrow \sigma^*(N-$   
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29 H), 7.14, 6.66 and 7.20 kcal  $mol^{-1}$  in the planar complexes, which is absent in the  
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31 perpendicular species.  
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39 Interesting trends are obtained too from the examination of the NBO occupation  
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41 numbers and the second order perturbation energies  $E^{(2)}$  of the hypervalent  $MI_2$  (T-  
42  
43 sh) and  $MBr_2$  (T-sh) complexes. As it can be seen from Tables 3-5, the occupation  
44  
45 numbers of the antibonding orbital  $\sigma^*(X-S)$  and the second order perturbation  
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47 energies  $E^{(2)}$  for the the charge-transfer interactions  $\sigma(X-S) \rightarrow \sigma^*(X-S)$  and  $LP_1(S) \rightarrow$   
48  
49  $\sigma^*(X-S)$ , 2.11 vs 2.94 and 3.0 vs 3.7 kcal  $mol^{-1}$  respectively, are lower for the  
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51 bromine complex. Therefore, they support the higher thermodynamic stability of  
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53  $MBr_2$  (T-sh) vs.  $MI_2$  (T-sh) as will be described next.  
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57  
58 Table 6 reports the calculated complexation enthalpies,  $\Delta H_r^{298}$ , and the  
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60 relative stabilities,  $\Delta E$ , of the isomeric molecular complexes studied. The  
complexation enthalpy at 298 K represents in the present work the difference in the

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3 gas-phase energy values including ZPE, BSSE and thermal energy corrections  
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5 between the molecular adduct and the separated fragments, i.e., the organic electron  
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7 donors M, M' and the dihalogens Br<sub>2</sub>, I<sub>2</sub>. The relative stability, ΔE, represents the  
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9 energy difference of the perpendicular geometries and the T-shaped hypervalent  
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11 isomers with respect to the planar configuration. The first inspection of Table 6  
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13 indicates bound systems and relatively large ΔH<sub>r</sub><sup>298</sup> values for most species, which  
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15 emphasize the significant stabilization and the strength of the halogen bonding  
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17 interaction of both CT and T-shaped molecular complexes of M and M' with X<sub>2</sub>.  
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19 More detailed examination shows various interesting differentiations in the  
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21 stabilization tendencies. Regarding the CT complexes, it is obvious that the additional  
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23 hydrogen bonding interaction produces a higher stability for the planar  
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25 conformations of both bromine and iodine CT complexes. Indeed, these results  
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27 reconfirm that the planar configurations allow both the main S • • I electron donor-  
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29 acceptor coupling and the additional hydrogen bonding interaction to operate most  
30  
31 effectively [10, 15, 18]. The calculations also demonstrate the lower stabilities of  
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33 the adducts involving the saturated organic framework with ΔE values roughly  
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35 twice the values for the methimazole derivatives. This tendency is expected on the  
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37 basis of the much stronger C-S bond in the parent saturated molecule, that  
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39 necessarily yields a weaker S • • I interaction. Of particular interest is the  
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41 comparison of the CT conformers with the T-shaped isomers, which shows a  
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43 reversion of the stability trends between the iodine and the bromine isomers. In the  
44  
45 iodine families the most stable adducts obtained are the planar CT complexes.  
46  
47 However, the bromine complexes exhibit an entirely opposite behavior and the T-  
48  
49 shaped adducts of both imidazoline and imidazolidine donors with Br<sub>2</sub> are the most  
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51 stable isomers. The reverse stabilization order which correlates well with the  
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53 structural and spectroscopic findings and the NBO analysis, may be attributed  
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3 macroscopically to the higher electronegativity of bromine. It may be reminded  
4 that the S-Br bond distance in the T-shaped hypervalent complexes almost assumes  
5 that the S-Br bond distance in the T-shaped hypervalent complexes almost assumes  
6 the S-Br bond distance value observed in bound systems. The larger electronegativity  
7 obviously strengthens the S-Br bonds more effectively than the S-I bonds and  
8 leads to a higher stabilization of the T-shaped bromine complexes.  
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15 Comparison with reported results verifies the above tendencies but deviations are  
16 observed in the actual values. For example, the complexation energy for M'-II  
17 (perp) is in excellent agreement with the diamino derivative result by Esseffar et al.  
18 [10]. The relative stabilities however, for the M complexes of iodine and  
19 bromine present deviations with the results of Aragoni et al. [17] for the dimethyl  
20 derivative, although they follow exactly the same trends. The discrepancy may lay  
21 in the secondary amidic interaction which is possible in the present compound and  
22 enhances the stabilization and which is absent in their N, N' dimethyl system. The  
23 different methodologies and the omission of the polarization functions on the  
24 halogens and of BSSE calculations may also contribute to the differences of the  
25 actual results.  
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#### 43 **4. Summary**

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45 We have carried out the computational investigation of the molecular complexes  
46 of the N-methyl imidazoline-2-thione and N-methyl imidazolidine-2-thione molecules  
47 with the dihalogens Br<sub>2</sub> and I<sub>2</sub>. The results confirm the higher stabilization of the  
48 planar CT conformers which exhibit a N-C-S-I torsional angle near 0° and allow the  
49 two kinds of interaction present in these adducts, namely the main electron donor-  
50 acceptor relation between the S and X atoms and the secondary hydrogen bonding  
51 between the inner halogen atom and the amidic hydrogen to operate most effectively.  
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60 The present calculations also demonstrate quantitatively the larger complexation

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3 enthalpies of the unsaturated thioamide complexes and the significant stabilization  
4 of the bromine T-shaped hypervalent complexes which are the most stable structures  
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6 in the bromine families.  
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## 10 11 12 13 **ACKNOWLEDGMENTS**

14  
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16 gratefully acknowledged.  
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Table 1. Selected structural parameters (Å, deg) for the molecular complexes of M, M' with the dihalogens X<sub>2</sub> (X=Br, I)

Species	N-H	C-S	S-X	X-X	S-X-X	C-S-X	N-C-S-X <sup>a</sup>
M, I <sub>2</sub>	1.013	1.670	----	2.653	----	----	----
M-II (plan)	1.019	1.695	2.811	2.771	177.7	98.2	0.0
M-II (perp)	1.014	1.692	2.829	2.766	177.1	89.8	98.1
		1.74 <sup>b</sup>	2.99 <sup>b</sup>	3.01 <sup>b</sup>	178.46 <sup>b</sup>	94.64 <sup>b</sup>	104.07 <sup>b</sup>
MI <sub>2</sub> (T-sh)	1.016	1.724	2.701	----	----	85.9	91.1
		1.78 <sup>b</sup>	2.91 <sup>b</sup>		175.70 <sup>b</sup>		90.0 <sup>b</sup>
M', I <sub>2</sub>	1.014	1.655	----	2.653	----	----	---
M'-II (plan)	1.018	1.679	2.842	2.758	178.3	100.1	18.1
M'-II (perp)	1.014	1.683	2.903	2.739	178.2	87.1	96.0
		1.665 <sup>c</sup>	3.044 <sup>c</sup>	2.773 <sup>c</sup>	177.0 <sup>c</sup>	99.6 <sup>c</sup>	
M'-I <sub>2</sub> (T-sh)	1.016	1.739	2.686	----	----	84.8	96.5
			2.703			83.9	95.8
M, Br <sub>2</sub>	1.013	1.670	----	2.289	----	----	----
M-BrBr (plan)	1.019	1.695	2.634	2.429	177.0	95.8	0.0
M-BrBr (perp)	1.014	1.692	2.667	2.416	176.8	89.7	106.8
		1.74 <sup>b</sup>	2.80 <sup>b</sup>	2.66 <sup>b</sup>	178.1 <sup>b</sup>	94.4 <sup>b</sup>	106.98 <sup>b</sup>
M-Br <sub>2</sub> (T-sh)	1.016	1.725	2.490	----	----	85.3	91.0
		1.78 <sup>b</sup>	2.71 <sup>b</sup>				95.06 <sup>b</sup>
M', Br <sub>2</sub>	1.014	1.655	----	2.289	----	----	----
M'-BrBr (plan)	1.017	1.678	2.671	2.410	177.9	98.3	15.5
M'-BrBr (perp)	1.013	1.680	2.784	2.372	177.7	85.4	98.8
M'-Br <sub>2</sub> (T-sh)	1.016	1.741	2.472	----	----	84.6	99.3
			2.494			83.2	99.0

<sup>a</sup> N here denotes the amidic N-H nitrogen atom, <sup>b</sup> Ref. [17] for the N, N' dimethyl-derivative, <sup>c</sup> Ref. [10] for the N,N' amidic derivative

Table 2 : Amidic stretching frequencies,  $\nu(\text{NH})$ , and frequency shifts,  $\Delta\nu(\text{NH})$ , ( $\text{cm}^{-1}$ )

Species	$\nu(\text{NH})$	$\Delta\nu(\text{NH})$	Species	$\nu(\text{NH})$	$\Delta\nu(\text{NH})$
M	3669.6	-			
M-II (plan)	3565.9	103.7	M-BrBr (plan)	3572.6	97.0
		116.7 <sup>a</sup> , 90.0 <sup>b</sup>			
M- II (perp)	3650.4	19.2	M-BrBr (perp)	3653.9	15.7
MI <sub>2</sub> (T-sh)	3634.7	34.9	MBr <sub>2</sub> (T-sh)	3636.8	32.8
M'	3639.0	-			
M'-II (plan)	3582.5	56.5, 60 <sup>c</sup>	M'-BrBr (plan)	3589.7	49.3
M'-II (perp)	3651.9	12.9	M'-BrBr (perp)	3651.6	12.6
M'I <sub>2</sub> (T-sh)	3626.8	12.2	M'Br <sub>2</sub> (T-sh)	3623.9	15.1

<sup>a</sup> Ref.[13], <sup>b</sup> Ref. [8], <sup>c</sup> [29]

Table 3 : The occupation numbers of NBOs in atomic units for iodine complexes

	M-II (perp)	M'-II (perp)	M-II (plan)	M'-II( plan)	M	M'
$\sigma$ (I-I)	1.9953	1.9959	1.9948	1.9949	-----	-----
$\sigma_1$ (C-S)	1.9848	1.9832	1.9849	1.9758	1.9957	1.9941
$\sigma_2$ (C-S)	-----	1.8554	-----	1.9148	1.9856	1.9850
LP <sub>1</sub> (S)	1.9765	1.9767	1.9806	1.9801	1.9882	1.9874
LP <sub>2</sub> (S)	1.9042	1.9085	1.7768	1.7663	1.8945	1.8994
LP <sub>3</sub> (S)	1.6259	-----	1.7173	-----	-----	-----
	(5.5066)	(3.8852)	(5.4747)	(3.7465)		
LP <sub>1</sub> (I)	1.9986	1.9989	1.9976	1.9975	-----	-----
LP <sub>2</sub> (I)	1.9972	1.9975	1.9969	1.9968	-----	-----
LP <sub>3</sub> (I)	1.9906	1.9898	1.9814	1.9839	-----	-----
LP(N5)	1.6182	1.7624	1.6215	1.7607	1.6524	1.7982
LP(N3)	-----	1.7116	-----	1.7321	1.6230	1.7480
N5-H	1.9895	1.9866	1.9887	1.9854	1.9901	1.9858
$\sigma^*$ (I-I)	0.1885	0.1479	0.2030	0.1845	-----	-----
$\sigma^*$ (N-H)	0.0116	0.0122	0.0235	0.0227	0.0114	0.0121
	MI <sub>2</sub> (T-sh)		M'I <sub>2</sub> (T-sh)		M	M'
$\sigma$ (I-S)	1.9492		1.9407		-----	-----
$\sigma_1$ (C-S)	1.9844		1.9821		1.9957	1.9941
$\sigma_2$ (C-S)	-----		-----		1.9856	1.9850
LP <sub>1</sub> (S)	1.9918		1.9918		1.9882	1.9874
LP <sub>2</sub> (S)	1.9279		1.9347		1.8945	1.8994
LP <sub>3</sub> (S)	-----		-----		-----	-----
	(3.9197)		(3.9265)			
LP <sub>1</sub> (I)	1.9995		1.9992		-----	-----
LP <sub>2</sub> (I)	1.9972		1.9983		-----	-----
LP <sub>3</sub> (I)	1.9775		1.9727		-----	-----
LP <sub>4</sub> (I)	1.4171		1.4251			
LP(N5)	1.5760		1.7373		1.6524	1.7982
LP(N3)	-----		-----		1.6230	1.7480
N5-H	1.9890		1.9835		1.9901	1.9858
$\sigma^*$ (I-S)	0.5252		0.5065		-----	-----
$\sigma^*$ (N-H)	0.0113		0.0127		0.0114	0.0121

Table 4 : The occupation numbers of NBOs in atomic units for bromine complexes

	M-BrBr (perp)	M-BrBr (plan)	M	
$\sigma(\text{Br-Br})$	1.9960	1.9958	-----	
$\sigma_1(\text{C-S})$	1.9847	1.9856	1.9957	
$\sigma_2(\text{C-S})$	-----	-----	1.9856	
$\text{LP}_1(\text{S})$	1.9781	1.9820	1.9882	
$\text{LP}_2(\text{S})$	1.8948	1.7749	1.8945	
$\text{LP}_3(\text{S})$	1.6086	1.6681	-----	
	(5.4815)	(5.4250)		
$\text{LP}_1(\text{Br})$	1.9985	1.9977	-----	
$\text{LP}_2(\text{Br})$	1.9976	1.9974	-----	
$\text{LP}_3(\text{Br})$	1.9918	1.9828	-----	
$\text{LP}(\text{N5})$	1.6208	1.6204	1.6524	
$\text{LP}(\text{N3})$	-----	-----	1.6230	
$\text{N5-H}$	1.9895	1.9887	1.9901	
$\sigma^*(\text{Br-Br})$	0.2080	0.2370	-----	
$\sigma^*(\text{N-H})$	0.0116	0.0220	0.0114	
	$\text{MBr}_2(\text{T-sh})$	$\text{M}'\text{Br}_2(\text{T-sh})$	M	M'
$\sigma(\text{Br-S})$	1.9610	1.9566	-----	-----
$\sigma_1(\text{C-S})$	1.9834	1.9811	1.9957	1.9941
$\sigma_2(\text{C-S})$	-----	-----	1.9856	1.9850
$\text{LP}_1(\text{S})$	1.9920	1.9919	1.9882	1.9874
$\text{LP}_2(\text{S})$	1.9283	1.9334	1.8945	1.8994
$\text{LP}_3(\text{S})$	-----	-----	-----	-----
	(3.9203)	(3.9253)		
$\text{LP}_1(\text{Br})$	1.9980	1.9981	-----	-----
$\text{LP}_2(\text{Br})$	1.9970	1.9976	-----	-----
$\text{LP}_3(\text{Br})$	1.9756	1.9706	-----	-----
$\text{LP}_4(\text{Br})$	1.4914	1.5009		
$\text{LP}(\text{N5})$	1.5744	1.7381	1.6524	1.7982
$\text{LP}(\text{N3})$	-----	-----	1.6230	1.7480
$\text{N5-H}$	1.9889	1.9827	1.9901	1.9858
$\sigma^*(\text{Br-S})$	0.4508	0.4304	-----	-----
$\sigma^*(\text{N-H})$	0.0113	0.0113	0.0114	0.0121

Table 5  
The second order perturbation energies  $E^{(2)}$  (kcal/mol) corresponding to the main charge transfer interactions

## Iodine complexes

Donor	Acceptor	M-II(plan)	M-II(perp)
LP <sub>3</sub> (S)	N2-C1	16.08	78.73
LP <sub>3</sub> (S)	N5-C1	6.53	0.55
LP <sub>3</sub> (S)	I-I	64.37 (86.98) <sup>a</sup>	53.17 (132.45) <sup>a</sup>
LP <sub>3</sub> (I)	N-H	7.14	-----

Donor	Acceptor	M'-II(plan)	M'-II(perp)
LP <sub>2</sub> (S)	N2-C1	14.45	13.11
LP <sub>2</sub> (S)	N5-C1	6.38	15.20
LP <sub>2</sub> (S)	I-I	35.70 (56.53) <sup>a</sup>	0.85 (29.16) <sup>a</sup>
LP <sub>3</sub> (I)	N-H	6.66	-----

Donor	Acceptor	MI <sub>2</sub> (T-sh)	
S-I	LP <sub>4</sub> (I)	7.82	7.45
S-I	S-I	2.94	2.55
S-I	N2-C1	20.33	24.48
LP <sub>3</sub> (I)	C1-N5	4.3	5.3
LP <sub>1</sub> (S)	S-I	3.7	3.36
LP <sub>1</sub> (S)	C1-N2	3.09	2.49
LP <sub>1</sub> (S)	C1-N5	3.18	2.96

## Bromine complexes

Donor	Acceptor	M-BrBr(plan)	M-BrBr(perp)
LP <sub>3</sub> (S)	N2-C1	13.97	80.00
LP <sub>3</sub> (S)	N5-C1	8.23	1.04
LP <sub>3</sub> (S)	Br-Br	73.97 (96.17) <sup>a</sup>	56.77 (137.81) <sup>a</sup>
LP <sub>3</sub> (Br)	N-H	7.2	-----

Donor	Acceptor	MBr <sub>2</sub> (T-sh)	M'Br <sub>2</sub> (T-sh)
S-Br	LP <sub>4</sub> (Br)	7.06	-----
S-Br	S-Br	2.11	1.80
S-Br	N2-C1	16.48	17.53
LP <sub>3</sub> (Br)	C1-N5	5.17	6.15
LP <sub>1</sub> (S)	S-Br	3.0	2.62
LP <sub>1</sub> (S)	C1-N2	2.95	2.36
LP <sub>1</sub> (S)	C1-N5	3.08	2.85

<sup>a</sup> Sum of energies  $E^{(2)}$  corresponding to the main delocalization of sulfur lone pairs

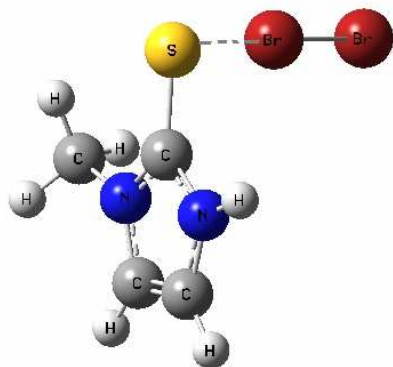
Table 6 : Complexation enthalpies,<sup>a</sup>  $\Delta H_r^{298}$ , and relative stabilities,<sup>a</sup>  $\Delta E$ , in kJ mol<sup>-1</sup> for M-X<sub>2</sub>, M'-X<sub>2</sub> molecular complexes (X=I,Br) including BSSE corrections

Species	$\Delta H_r^{298}$	$\Delta E$	Species	$\Delta H_r^{298}$	$\Delta E$
M-II (plan)	-48.3	0.0	M-BrBr (plan)	-41.5	0.0
M- II (perp)	-46.7	1.6	M-BrBr (perp)	-38.8	2.7
MI <sub>2</sub> (T-sh)	-38.0	10.3 15.5 <sup>b</sup>	MBr <sub>2</sub> (T-sh)	-61.2	-19.7 -8.8 <sup>b</sup>
M'-II (plan)	-41.7	0.0	M'-BrBr (plan)	-36.2	0.0
M'-II (perp)	-38.0 -34.7 <sup>c</sup>	3.7	M'-BrBr (perp)	-28.6	7.6
M'I <sub>2</sub> (T-sh)	-15.7	26.0	M'Br <sub>2</sub> (T-sh)	-43.1	-6.9

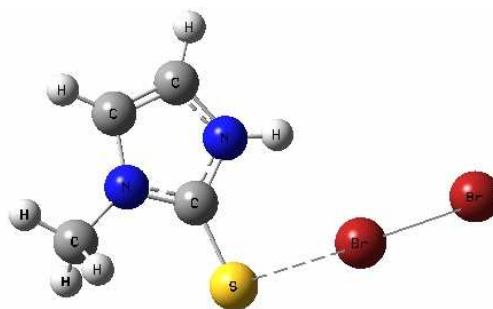
<sup>a</sup> See text for the definition of these quantities, <sup>b</sup> Results of Ref. [17] for the dimethyl derivative, not including BSSE corrections, <sup>c</sup> Result of ref. [10] for the diamino derivative, including BSSE corrections and the  $\Delta(PV)$  term



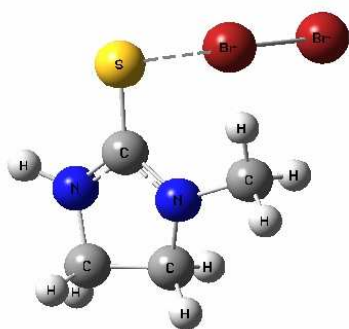
Figure 1. Structures of bromine complexes with M and M' organic frameworks



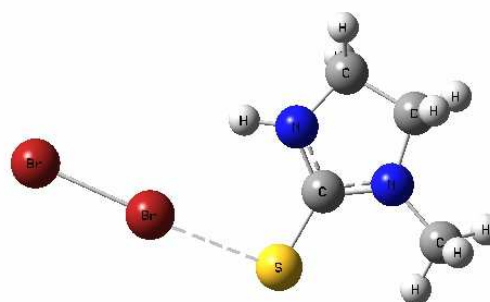
**M-Br-Br perp**



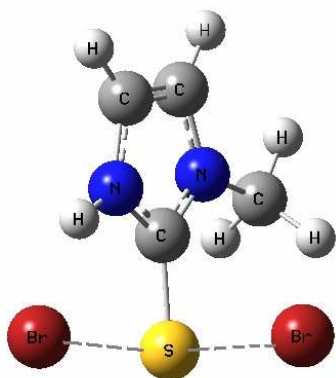
**M-Br-Br planar**



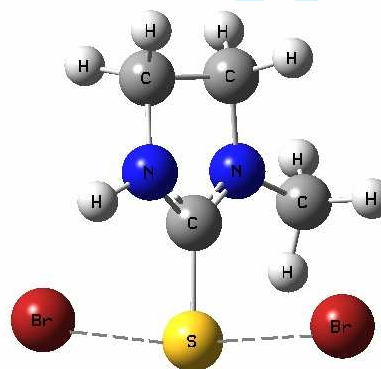
**M'-Br-Br perp**



**M'-Br-Br planar**



**MBr<sub>2</sub> T-shaped**



**M'Br<sub>2</sub> T-shaped**