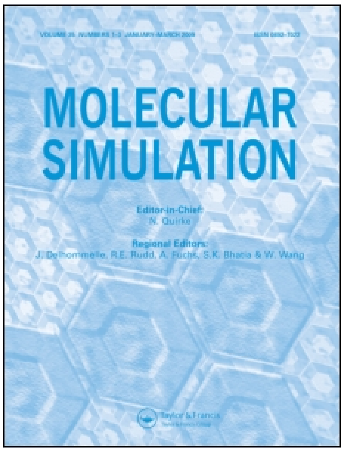

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Computational characterisation of the charge-transfer and T-shaped molecular complexes of *N*-methyl imidazoline-2-thione and *N*-methyl imidazolidine-2-thione with the dihalogens Br_2 and I_2

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The computational characterisation of the molecular complexes of *N*-methyl imidazoline-2-thione (methimazole) and the related saturated analogue *N*-methyl imidazolidine-2-thione with Br_2 and I_2 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 (CT) type adducts, possible in two stereoisomeric conformations depending on the direction of the X_2-axis, either planar or perpendicular to the NCS plane. The second kind corresponds to T-shaped hypervalent complexes in which sulphur is connected to both the X atoms forming the linear X—S—X arrangement. The structural changes, the spectroscopic findings, the natural bond orbital analysis and the examination of the molecular orbital 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 basis set superposition error corrections, which show the larger stabilisation 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 characterised by intermolecular distances shorter than the range of van der Waals distances. As it has recently been reviewed [1–3], the tendency of diiodine to form complexes with Lewis bases has been repeatedly recognised 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 characterised 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···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 CT 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 recognised nowadays as the most important non-covalent interaction after hydrogen bonding [1–3]. It is largely an electrostatic phenomenon and the more electronegative the element to which the halogen is bound to, for example O or N, the better the electron acceptor becomes. Fluorine has proved to be a poor electron acceptor, forming very weak halogen bonds, if at all. In the numerous investigations, several series of simple molecules have been studied as Lewis bases B, among them CO, C_2H_2, C_2H_4, H_2O, H_2S HCN, NH_3, $N(CH_3)_3$, CH_3CN, H_2CO, PH_3, benzene derivatives, furan, thiophene and saturated rings such as oxirane and thiirane [1–3]. Current interest into halogen-bonded complexes has been expanded to include organohalogen and inorganic halide acceptors [1–7]. However, the dihalogens (X_2) and interhalogens (XY) continue to attract attention and the study of diiodine complexes with organic frameworks involving sulphur and selenium electron donors still receives intensive consideration because of the variety of the potential biological, pharmaceutical and

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electronic material applications of these complexes [8–19]. As pointed out by Pennington et al. [3]: ‘among the many applications involving X_2 and XY halogen bonding, this type of interaction is increasingly being discovered to play a significant role in biochemical systems, particularly in thyroid chemistry’. While halogen bonding involving the halogenated thyroid enzymes is often the focus of studies in this area, the role of I_2 is also of interest since it is closely related to numerous investigations into the interaction of antithyroid drugs with I_2 [3]. Indeed, a prominent member among the group of sulphur electron-donor compounds is *N*-methyl imidazoline-2-thione, commercially available as methimazole, which has been widely used in the treatment of hyperthyroidism. Its diverse properties have been attributed to the high coordination ability of the RN—C(═S)—NR′ heterocyclic thioamide group to both metallic and non-metallic elements, leading to stable electron-donor–acceptor complexes. The crystallographic and theoretical studies have established two kinds of connectivity for the dihalogen complexes of methimazole and related organic frameworks. The first corresponds to CT-type adducts containing the linear S—X—X geometry and are possible in two stereoisomeric conformations with the X_2 molecular axis being either planar or perpendicular with respect to the NCS plane. The second type corresponds to the T-shaped hypervalent complexes in which sulphur is connected to both the X atoms forming the linear X—S—X arrangement.

In the present work, a detailed computational study is carried out on the structural and energy characteristics of the CT and T-shaped molecular complexes of *N*-methyl imidazoline-2-thione (denoted hereafter as M) and the related saturated analogue *N*-methyl imidazolidine-2-thione (denoted as M′) with Br_2 and I_2. The comparison between the various conformeric isomers and the bromine and iodine complexes shows interesting effects on the stabilisation of the particular type of connectivity that may be attributed at a first glance to the different electronegativity and other factors such as a secondary hydrogen bonding interaction. However, natural bond orbital (NBO) calculations are performed in order to get a deeper insight into the nature of the bonding and the strength of the intermolecular interactions and obtain, in this way, a good evaluation of the delocalisation effects. Despite several interesting investigations on methimazole derivatives already reported [17], we believe that the present work exhibits many differences compared with previous studies and several new features are examined. For example, in contrast to previous reports where both the nitrogen atoms of the methimazole ring bear each a methyl group [17], our system contains one nitrogen atom bound to a methyl group and the other connected to an H atom. Thus, the present model system allows the additional investigation of a possible secondary hydrogen–halogen interaction not available in other reported cases [17]. Our study also extends to the saturated analogue, and it allows a comparison of the strength of the CT interaction in both the imidazoline and imidazolidine organic frameworks that is not reported previously. There are differences in the methodologies too, which will be analysed in Section 2. We would just like to mention here only the basis set superposition error (BSSE) energy corrections which have been performed in the present work and which are considered to be very important for the proper evaluation of the energy results in non-covalent interacting systems. Therefore, we believe that there are many new points considered in the present study, and the detailed comparison with other reported computational results on methimazole derivatives and similar systems would present a lot of interest.

2. Computational details

While the general features of halogen bonding are by now well established, it is becoming a challenge to predict the molecular parameters of halogen-bonded complexes and verify the experimentally observed trends using high-level quantum mechanical computational techniques. The basic issue in these studies is the search of reliable computational techniques and appropriate basis sets to describe such systems as best as possible taking into account their large size and the corresponding computational cost.

The electronic molecular structure calculations have been performed using the Gaussian 98 series of programs [20]. The restricted second-order Møller–Plesset (MP2) level of theory has been employed in combination with different basis sets for the various atoms involved. The halogens have been treated using the orbital-adjusted ECP plus DZ effective core potential method of Hay and Wadt, i.e. the LANL2DZ basis set [21]. It is worth noting here the need, often stressed in the literature, for the use of additional polarisation functions in combination with the valence LANL2DZ basis set in order to achieve a more accurate description of the halogen atom in halogen-bonded CT complexes [22,23]. Thus, additional polarisation functions have been employed to increase the halogen valence basis sets in order to describe as best as possible the polarisation of the halogen atoms [24]. Specifically, the Br valence basis set was augmented with two *d* and one *f* polarisation functions from the cc-pvTZ basis set [25]. For the iodine treatment, two *d* and one *f* polarisation functions were taken from the Stuttgart–Bonn ECPnMDF (Dirac–Fock) relativistic potential [26]. We believe that the enlargement of the halogen valence-bond LANL2DZ basis set with additional polarisation functions consists of a significant improvement over previously reported calculations on similar methimazole systems. The 6-31G+(d) basis set was used for sulphur in order to account for a possible diffusion of its valence functions due to the non-covalent halogen bonding interaction and the 6-31G(d,p) one for the other atoms. Considering the large size of the molecules under investigation and the large number of atoms involved, the level of theory employed in the present study should be satisfactory and comparable or even higher than the levels of theory employed in the study of similar systems by other workers.

As described in Section 1, the present work aims at investigating molecular interaction energies of relatively weakly bonded gas-phase systems. For such systems, the consideration of the limited basis set effects is a necessary requirement arising from the superposition of these finite basis sets in the optimisation procedure, due to the different number of basis functions considered in the complex and the monomer optimisations. Thus, the BSSE correction is an important issue in the proper treatment of non-covalent intermolecular interactions, and it has been shown to be sizably large for a series of relevant species [10]. Hence, BSSE calculations following the functional counterpoise scheme [27] have been additionally carried out for the present molecular complexes, in order to amend properly the computed binding energies and relative stabilities. This is another difference with several reported calculations on methimazole-related systems [17] that, in our opinion, give additional merit to the present results.

3. Structural and spectroscopic results

Tables 1 and 2 show the calculated structural and spectroscopic results and compare with literature data. Figure 1 displays the optimised structures of the adducts between the organic donors and the dihalogens only for the case X = Br since the iodine complexes present similar geometries. The results are in good agreement with the reported experimental evidence and previous theoretical calculations and the comparison with density functional theory (DFT) calculations (Table 1) reconfirms the tendency of the MP2 methodology to predict tighter structures than the density functional theory techniques [17]. Two types of stereoisomeric CT complexes have been obtained between *N*-methyl imidazoline-2-thione, denoted as M, and the related saturated analogue *N*-methyl imidazolidine-2-thione, denoted as M′, and the dihalogens. Both configurations feature a collinear S—X—X geometry. In the first type, the torsional angle NCSX (where N is the amidic N—H nitrogen atom) around the C═S bond is close to 0° for the M—XX species or a little disturbed in the range 14°–18° for the case of the M′—XX complexes, indicating that the dihalogen molecular axis is slightly displaced off the thioamide plane. The second type presents a perpendicular arrangement of the dihalogen molecular axis with respect to the thioamide plane and exhibits a NCSX torsional angle ranging from 96° to 99°. The corresponding geometries are denoted hereafter

Table 1. Selected structural parameters (Å, deg) for the molecular complexes of M, M′ with the dihalogens X_2 (X = Br, I).

Species	N—H	C—S	S—X	X—X	S—X—X	C—S—X	N—C—S—X[a]
M, I_2	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[b]	2.99[b]	3.01[b]	178.46[b]	94.64[b]	104.07[b]
MI_2 (T-sh)	1.016	1.724	2.701	–	–	85.9	91.1
		1.78[b]	2.91[b]		175.70[b]		90.0[b]
M′, I_2	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[c]	3.044[c]	2.773[c]	177.0[c]	99.6[c]	
M′—I_2 (T-sh)	1.016	1.739	2.686	–	–	84.8	96.5
			2.703			83.9	95.8
M, Br_2	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[b]	2.80[b]	2.66[b]	178.1[b]	94.4[b]	106.98[b]
M—Br_2 (T-sh)	1.016	1.725	2.490	–	–	85.3	91.0
		1.78[b]	2.71[b]				95.06[b]
M′, Br_2	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_2 (T-sh)	1.016	1.741	2.472	–	–	84.6	99.3
			2.494			83.2	99.0

[a] N denotes the amidic N—H nitrogen atom. [b] [17] for the *N,N*′-dimethyl derivative. [c] [10] for the *N,N*′-amidic derivative.

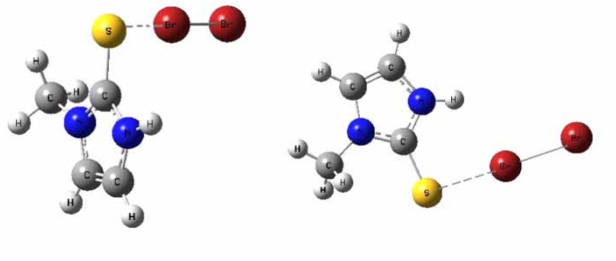
Table 2. Amidic stretching frequencies, ν(NH), and frequency shifts, $\Delta\nu$(NH) (cm^{-1}).

Species	ν(NH)	$\Delta\nu$(NH)	Species	ν(NH)	$\Delta\nu$(NH)
M	3669.6	–			
M—II (plan)	3565.9	103.7 116.7[a], 90.0[b]	M—BrBr (plan)	3572.6	97.0
M—II (perp)	3650.4	19.2	M—BrBr (perp)	3653.9	15.7
$\mathrm{MI_2}$ (T-sh)	3634.7	34.9	$\mathrm{MBr_2}$ (T-sh)	3636.8	32.8
$\mathrm{M'}$	3639.0	–			
$\mathrm{M'}$—II (plan)	3582.5	56.5, 60[c]	$\mathrm{M'}$—BrBr (plan)	3589.7	49.3
$\mathrm{M'}$—II (perp)	3651.9	12.9	$\mathrm{M'}$—BrBr (perp)	3651.6	12.6
$\mathrm{M'I_2}$ (T-sh)	3626.8	12.2	$\mathrm{M'Br_2}$ (T-sh)	3623.9	15.1

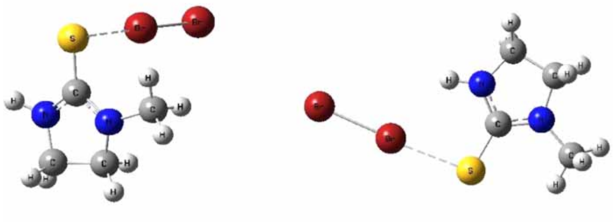
[a] [13]. [b] [8]. [c] [29].

as planar and perpendicular, respectively. The T-shaped hypervalent isomers present a near perpendicular arrangement of the X—S—X line relative to the thioamide plane.

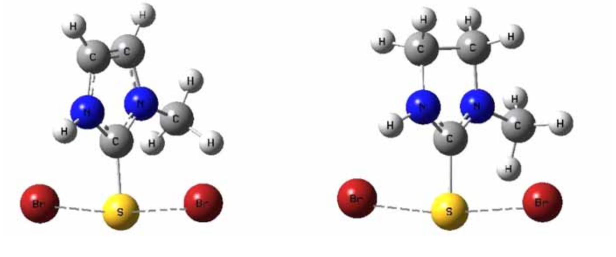
The three isomeric species of each family show several interesting geometrical features which may be correlated to a certain extent with the NBO occupation numbers and the energy stabilisation tendencies. The main important structural variation is the significant elongation of the C—S bond distance of the order of 0.25 Å in both conformations of iodine and bromine CT complexes compared to the free M, $\mathrm{M'}$ species. This elongation becomes even more pronounced in the case of the T-shaped hypervalent adducts where the C—S bond distance increases by about 0.5–0.8 Å compared to the free organic frameworks. Another interesting change is the significant expansion of the X—X bond in the CT adducts, particularly in the planar complexes. The S—X distance also shows important variations and decreases in the planar configurations relative to the perpendicular structures, reducing further in the T-shaped complexes. Specifically, the S—X length decreases by 0.110 Å from M—II (planar) to $\mathrm{MI_2}$ (T-sh), 0.156 Å from $\mathrm{M'}$—II (planar) to $\mathrm{M'I_2}$ (T-sh), 0.144 Å from M—BrBr (planar) to $\mathrm{MBr_2}$ (T-sh) and 0.199 Å from $\mathrm{M'}$—BrBr (planar) to $\mathrm{M'Br_2}$ (T-sh). The saturated imidazolidine T-shaped complexes with both dihalogens slightly differentiate the two S—X distances leading to smaller S—X values for the X closer to the methylic N. It is interesting to mention here that the calculated S—Br distances obtained in the T-shaped complexes approach S—Br bond distances (similar, for example, to those of species like BrSSBr [28]), faster than the corresponding S—I bond lengths, with relevant consequences in the stabilisation of the corresponding adducts. Indeed, the larger reduction of the S—X distance in the bromine T-shaped hypervalent complexes, i.e. 0.144 and 0.199 Å for the bromine M and $\mathrm{M'}$ complexes relative to 0.110 and 0.156 Å for the iodine M and $\mathrm{M'}$ adducts, respectively, may be correlated with the higher electronegativity of bromine and may be the explanation for the larger stabilisation of the T-shaped adducts vs. the CT structures in the bromine family. This observation is supported by the examination of the NBO occupation numbers (see Section 4).



M–Br–Br (perp) M–Br–Br (planar)



M'–Br–Br (perp) M'–Br–Br (planar)



$\mathrm{MBr_2}$ (T-shaped) $\mathrm{M'Br_2}$ (T-shaped)

Figure 1. Structures of the bromine complexes with M and $\mathrm{M'}$ organic frameworks.

The N—H bond distance shows a mild increase upon complexation, particularly in the planar CT-type geometries, reflecting a possible additional interaction of the amidic hydrogen with the inner halogen atom, favoured mainly in the coplanar configurations. This secondary intramolecular hydrogen bonding interaction has also been observed in a large number of related systems [10], and it is much better demonstrated in the N—H stretching frequency shift that takes place upon complexation, resulting in the higher stabilisation of the planar configurations vs. the perpendicular arrangement, as we shall see next. The angular parameters show less pronounced differentiations between the planar and the perpendicular structures and the T-shaped isomers. We note that only the planar M′—XX configurations involve a small but non-negligible deviation from the planar geometry, 18.1° for M′—II and 15.5° for M′—BrBr planar CT complexes.

The main spectroscopic feature that emerges from the harmonic vibrational frequency analysis is the shift in the N—H stretching frequency observed in the IR spectra of the adducts compared to the free organic species (Table 2). This frequency shifting may be related to the slight extension of the amidic N—H bond in the planar M—XX, M′—XX complexes, discussed above, and implies the possible operation of an additional intramolecular NH···X hydrogen bonding interaction that contributes to the stabilisation of the planar complexes. Thus, the inner I atom and, to a much lesser extent, the inner Br atom, may be considered to show an amphoteric behaviour in the planar complexes acting additionally to a small extent as an electron donor to the acidic H of the amidic NH group and affecting the harmonic vibrational frequency. The calculated unscaled harmonic frequency shift $\Delta\nu(\mathrm{NH}) = 103.7\,\mathrm{cm}^{-1}$ for the M—II (planar) complex reproduces fairly close to the experimental value, $90\,\mathrm{cm}^{-1}$ [8], much closer than other computational studies [13] (Table 2), confirming the reliability of the level of theory employed in the present work. A good consistency is also observed between the $\Delta\nu$(NH) values of the M′—II complexes calculated in the present work, $\sim 60\,\mathrm{cm}^{-1}$, and the experimental results ranging from 52 to $61\,\mathrm{cm}^{-1}$ for the diiodine CT complexes of a series of compounds belonging to the imidazolidine family [29].

4. NBO analysis and energy–relative stability results

The NBO occupation numbers for the CT M—II, M′—II and M—BrBr (both conformers) and the hypervalent MX_2, $M'X_2$ (X = I, Br) T-shaped complexes are summarised in Tables 3 and 4. Table 5 displays the second-order

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′
σ(I—I)	1.9953	1.9959	1.9948	1.9949	–	–
σ_1(C—S)	1.9848	1.9832	1.9849	1.9758	1.9957	1.9941
σ_2(C—S)	–	1.8554	–	1.9148	1.9856	1.9850
LP_1(S)	1.9765	1.9767	1.9806	1.9801	1.9882	1.9874
LP_2(S)	1.9042	1.9085	1.7768	1.7663	1.8945	1.8994
LP_3(S)	1.6259	–	1.7173	–	–	–
	(5.5066)	(3.8852)	(5.4747)	(3.7465)		
LP_1(I)	1.9986	1.9989	1.9976	1.9975	–	–
LP_2(I)	1.9972	1.9975	1.9969	1.9968	–	–
LP_3(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
σ*(I—I)	0.1885	0.1479	0.2030	0.1845	–	–
σ*(N—H)	0.0116	0.0122	0.0235	0.0227	0.0114	0.0121
	MI_2 (T-sh)		$M'I_2$ (T-sh)		M	M′
σ(I—S)	1.9492		1.9407		–	–
σ_1(C—S)	1.9844		1.9821		1.9957	1.9941
σ_2(C—S)	–		–		1.9856	1.9850
LP_1(S)	1.9918		1.9918		1.9882	1.9874
LP_2(S)	1.9279		1.9347		1.8945	1.8994
LP_3(S)	–		–			
	(3.9197)		(3.9265)			
LP_1(I)	1.9995		1.9992		–	–
LP_2(I)	1.9972		1.9983		–	–
LP_3(I)	1.9775		1.9727		–	–
LP_4(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
σ*(I—S)	0.5252		0.5065		–	–
σ*(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
σ(Br—Br)	1.9960	1.9958	–
σ_1(C—S)	1.9847	1.9856	1.9957
σ_2(C—S)	–	–	1.9856
LP_1(S)	1.9781	1.9820	1.9882
LP_2(S)	1.8948	1.7749	1.8945
LP_3(S)	1.6086 (5.4815)	1.6681 (5.4250)	–
LP_1(Br)	1.9985	1.9977	–
LP_2(Br)	1.9976	1.9974	–
LP_3(Br)	1.9918	1.9828	–
LP(N5)	1.6208	1.6204	1.6524
LP(N3)	–	–	1.6230
N5—H	1.9895	1.9887	1.9901
σ*(Br—Br)	0.2080	0.2370	–
σ*(N—H)	0.0116	0.0220	0.0114

	MBr_2 (T-sh)	$M'Br_2$ (T-sh)	M	M′
σ(Br—S)	1.9610	1.9566	–	–
σ_1(C—S)	1.9834	1.9811	1.9957	1.9941
σ_2(C—S)	–	–	1.9856	1.9850
LP_1(S)	1.9920	1.9919	1.9882	1.9874
LP_2(S)	1.9283	1.9334	1.8945	1.8994
LP_3(S)	– (3.9203)	– (3.9253)	–	–
LP_1(Br)	1.9980	1.9981	–	–
LP_2(Br)	1.9970	1.9976	–	–
LP_3(Br)	1.9756	1.9706	–	–
LP_4(Br)	1.4914	1.5009		
LP(N5)	1.5744	1.7381	1.6524	1.7982
LP(N3)	–	–	1.6230	1.7480
N5—H	1.9889	1.9827	1.9901	1.9858
σ*(Br—S)	0.4508	0.4304	–	–
σ*(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_3(S)	N2—C1	16.08	78.73
LP_3(S)	N5—C1	6.53	0.55
LP_3(S)	I—I	64.37 (86.98)[a]	53.17 (132.45)[a]
LP_3(I)	N—H	7.14	–
Donor	Acceptor	M′—II (plan)	M′II (perp)
LP_2(S)	N2—C1	14.45	13.11
LP_2(S)	N5—C1	6.38	15.20
LP_2(S)	I—I	35.70 (56.53)[a]	0.85 (29.16)[a]
LP_3(I)	N—H	6.66	–
Donor	Acceptor	MI_2 (T-sh)	
S—I	LP_4(I)	7.82	7.45
S—I	S—I	2.94	2.55
S—I	N2—C1	20.33	24.48
LP_3(I)	C1—N5	4.3	5.3
LP_1(S)	S—I	3.7	3.36
LP_1(S)	C1—N2	3.09	2.49
LP_1(S)	C1—N5	3.18	2.96
Bromine complexes			
Donor	Acceptor	M—BrBr (plan)	M—BrBr (perp)
LP_3(S)	N2—C1	13.97	80.00
LP_3(S)	N5—C1	8.23	1.04
LP_3(S)	Br—Br	73.97 (96.17)[a]	56.77 (137.81)[a]
LP_3(Br)	N—H	7.2	–
Donor	Acceptor	MBr_2 (T-sh)	$M'Br_2$ (T-sh)
S—Br	LP_4(Br)	7.06	–
S—Br	S—Br	2.11	1.80
S—Br	N2—C1	16.48	17.53
LP_3(Br)	C1—N5	5.17	6.15
LP_1(S)	S—Br	3.0	2.62
LP_1(S)	C1—N2	2.95	2.36
LP_1(S)	C1—N5	3.08	2.85

[a] Sum of the energies $E^{(2)}$ corresponding to the main delocalisation of sulphur lone pairs.

perturbation energies $E^{(2)}$ corresponding to the main CT interactions present.

The analysis of these data is in good agreement with the structural trends and the frequency shift calculations and gives interesting information about the nature and the strength of the halogen bonding. For instance, the occupation number of the σ_1(C—S) bonding orbital decreases in all cases upon complexation, reflecting the reduction of electron density due to the partial transfer to the S···X (X = I, Br) interaction. Comparison of the planar and perpendicular geometries is revealing too. The occupation number of the σ*(N—H) antibonding orbital increases upon complexation from 0.0114 in free M to 0.0116 in M—II (perp) and 0.0235 in M—II (plan) with similar results for the M′—II and M—BrBr complexes. The increase is most pronounced in the planar configurations and is an additional evidence for a possible, secondary interaction of the hydrogen bonding type between the amidic hydrogen and the halogen atom, favoured in the planar geometry. It is readily manifested in the larger stabilisation of the planar conformers, as we shall see in the next paragraph. On the other hand, the smaller increase of the σ*(N—H) antibonding orbital occupation number in the M—BrBr (plan), i.e. from 0.0114 to 0.0220, vs. the iodine planar complexes is a clear indication of the poorer capacity of bromine, compared to iodine, to play an amphoteric role, i.e. to act primarily as an electron acceptor for sulphur and secondarily as an electron donor for the amidic hydrogen due to its higher electronegativity. This feature is reflected too in the lower ΔH_r^{298} value of M—BrBr (plan). Another relevant characteristic is the larger σ*(X—X) antibonding orbital occupation number in the coplanar vs. the perpendicular arrangement, which can be rationalised in terms of the CT interactions between orbitals. As shown in Table 5, the S lone pair, $LP_3(S)$, participates as a donor and the σ*(X—X) antibond as the acceptor in a strong intermolecular CT interaction, $LP_3(S) \rightarrow \sigma^*(X—X)$, for which the corresponding energies $E^{(2)}$ for M—II (plan) and MBrBr (plan) (64.37 and 73.97 kcal mol^{-1}, respectively) are much larger than that for MII (perp) and MBrBr (perp) (53.17 and 56.77 kcal mol^{-1}). Of interest is also the larger occupation number $LP_3(S)$ in both planar iodine and bromine CT complexes vs. the perpendicular conformers and the non-negligible CT energy $E^{(2)}$ for $LP_3(X) \rightarrow \sigma^*(N—H)$, 7.14, 6.66 and 7.20 kcal mol^{-1} in the planar complexes, which is absent in the perpendicular species.

Interesting trends are obtained too from the examination of the NBO occupation numbers and the second-order perturbation energies $E^{(2)}$ of the hypervalent MI_2 (T-sh) and MBr_2 (T-sh) complexes. As it can be seen from Tables 3–5, the occupation numbers of the antibonding orbital σ*(X—S) and the second-order perturbation energies $E^{(2)}$ for the CT interactions $\sigma(X—S) \rightarrow \sigma^*(X—S)$ and $LP_1(S) \rightarrow \sigma^*(X—S)$, 2.11 vs. 2.94 and 3.0 vs. 3.7 kcal mol^{-1}, respectively, are lower for the bromine complex. Therefore, they support the higher thermodynamic stability of MBr_2 (T-sh) vs. MI_2 (T-sh) as will be described next.

Table 6 reports the calculated complexation enthalpies, ΔH_r^{298}, and the relative stabilities, ΔE, of the isomeric molecular complexes studied. In the present work, the difference in the complexation enthalpy at 298 K represents the gas-phase energy values including zero point energy (ZPE), BSSE and thermal energy corrections between the molecular adduct and the separated fragments, i.e. the organic electron donors M, M′ and the dihalogens Br_2, I_2. The relative stability, ΔE, represents the energy difference between the perpendicular geometries and the T-shaped hypervalent isomers with respect to the planar configuration. The first inspection of Table 6 indicates bound systems and relatively large ΔH_r^{298} values for most species, which emphasise the significant stabilisation and the strength of the halogen bonding interaction of both CT and T-shaped molecular complexes of M and M′ with X_2. A more detailed examination shows various interesting differentiations in the stabilisation tendencies. Regarding the CT complexes, it is obvious that the additional hydrogen bonding interaction produces a higher stability for the planar conformations of both bromine and iodine CT complexes. Indeed, these results reconfirm that the planar configurations allow both the main S···I electron-donor–acceptor coupling and the additional hydrogen bonding interaction to operate most effectively [10,15,18]. The calculations also demonstrate the lower stabilities of the adducts involving the saturated organic framework, with ΔE values roughly twice the values for the methimazole derivatives. This tendency is expected on the basis of the much stronger C—S bond in the parent saturated molecule, which necessarily yields a weaker S···I interaction. Of particular interest is the comparison of the CT conformers with the T-shaped isomers, which shows a reversion of the stability trends between the iodine and the bromine isomers. In the iodine families, the most stable adducts obtained are the planar CT complexes. However, the bromine complexes exhibit an entirely opposite behaviour and the T-shaped adducts of both imidazoline and imidazolidine donors with Br_2 are the most stable isomers. The reverse stabilisation order, which correlates well with the structural and spectroscopic findings and the NBO analysis, may be attributed macroscopically to the higher electronegativity of bromine. It may be reminded that the S—Br bond distance in the T-shaped hypervalent complexes almost assumes the S—Br bond distance value observed in bound systems. The larger electronegativity obviously strengthens the S—Br bonds more effectively than the S—I bonds and leads to a higher stabilisation of the T-shaped bromine complexes.

A comparison with reported results verifies the above tendencies, but deviations are observed in the actual values. For example, the complexation energy for M′—II (perp) is in excellent agreement with the diamino derivative result by Esseffar et al. [10]. The relative

Table 6. Complexation enthalpies,[a] ΔH_r^{298}, and relative stabilities,[a] ΔE, in kJ mol^{-1} for M—X_2, M′—X_2 molecular complexes (X = I, Br) including the BSSE corrections.

Species	ΔH_r^{298}	ΔE	Species	ΔH_r^{298}	ΔE
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_2 (T-sh)	−38.0	10.3 15.5[b]	MBr_2 (T-sh)	−61.2	−19.7 −8.8[b]
M′—II (plan)	−41.7	0.0	M′—BrBr (plan)	−36.2	0.0
M′—II (perp)	−38.0 −34.7[c]	3.7	M′—BrBr (perp)	−28.6	7.6
$M'I_2$ (T-sh)	−15.7	26.0	$M'Br_2$ (T-sh)	−43.1	−6.9

[a] See text for the definition of these quantities. [b] Results of [17] for the dimethyl derivative, not including the BSSE corrections. [c] Result of [10] for the diamino derivative, including the BSSE corrections and the ΔPV term.

stabilities, however, for the M complexes of iodine and bromine present deviations from the results of Aragoni et al. [17] for the dimethyl derivative, although they follow exactly the same trends. The discrepancy may lie in the secondary amidic interaction which is possible in the present compound and enhances the stabilisation, and which is absent in their *N*,*N*′-dimethyl system. The different methodologies and the omission of the polarisation functions on the halogens and of the BSSE calculations may also contribute to the differences of the actual results.

5. Summary

We have carried out the computational investigation of the molecular complexes of the *N*-methyl imidazoline-2-thione and *N*-methyl imidazolidine-2-thione molecules with the dihalogens Br_2 and I_2. The results confirm the higher stabilisation of the planar CT conformers which exhibit an N—C—S—I torsional angle near 0° and allow the two kinds of interaction present in these adducts, namely the main electron-donor–acceptor relation between the S and X atoms and the secondary hydrogen bonding between the inner halogen atom and the amidic hydrogen to operate most effectively. The present calculations also quantitatively demonstrate the larger complexation enthalpies of the unsaturated thioamide complexes and the significant stabilisation of the bromine T-shaped hypervalent complexes which are the most stable structures in the bromine families.

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