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# A solid-state structural and theoretical study on the 1 : 1 addition compounds of thioethers with dihalogens and interhalogens I–X (X = I, Br, Cl)†

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Two new thioether interhalogen adducts, $(PhCH_2)_2S\cdot ICl$ (**1**) and $(PhCH_2)_2S\cdot IBr$ (**2**) have been prepared and characterised in the solid-state, the prior being the first crystallographically characterised example of a thioether ICl charge transfer complex. Theoretical calculations have been carried out on a related series of thioether IX adducts (X = F, Cl, Br, I) and reveal the computed geometries for these systems, in particular the S–I and I–X distances, to vary significantly based on the choice of basis set and type of density functional hybridisation model employed. In order to model these electron rich adducts accurately we demonstrate the importance of using high quality basis sets and density functional hybridisation models which are able to handle electron correlation accurately, and also the importance of lattice effects.

## Introduction

The ability of organic molecules containing Group 15 or 16 donor atoms to form addition complexes with dihalogen and interhalogen acceptors is well recognised, and these so called charge transfer[1] complexes have been investigated for their potential applications in the oxidation of unactivated metal powders, as reagents for organic syntheses and as synthetic antithyroids.[2] In addition, complexes between diiodine or iodine monochloride and n or π donors have recently been used to probe the dynamics and structure of bimolecular electron transfer processes at the femtosecond time-scale.[3]

One of the first dihalide addition complexes to be structurally characterised was that of diiodide with dibenzyl sulfide which was reported by Rømming in 1960.[4] X-Ray crystallography revealed $(PhCH_2)_2S\cdot I_2$ to adopt a charge transfer spoke structure with a close to linear S–I–I arrangement, a S–I distance of 2.78(2) Å and an elongated I–I bond [2.819(9) Å].[4] Subsequently, the X-ray studies of a range of diiodide adducts with thioether crown complexes has also been reported, all of which exhibit an essentially similar spoke structure with S–I and I–I bond distances in the range 2.654(3) to 2.880(2) Å [mean 2.782 Å] and 2.674(3) to 2.902(2) Å [mean 2.798 Å], respectively.[5] In addition, several crystallographically characterised examples of iodine monobromide adducts with crown thioethers have been reported, again exhibiting spoke structures with approximately linear S–I–Br arrangements.[6,7] These IBr adducts were shown to form stronger complexes with shorter S–I distances [range 2.618(2) to 2.687(2) Å] than those observed in the analogous $I_2$ complexes, attributable to the superior acceptor ability of IBr with respect to $I_2$, and I–Br bond distances in the range 2.6445(12) to 2.7049(11) Å.[6,7] Prior to this paper, no crystallographically characterised thioether iodine monochloride adducts had been reported, although a recent theoretical study on $Et_2S\cdot ICl$ predicted a spoke structure in keeping with those of $R_2S$ with $I_2$ and IBr, and a S–I distance of between 2.995 and 3.166 Å.[8]

The nature of the electron donor–acceptor interaction in these Group 16–dihalogen and interhalogen complexes has been investigated in several theoretical studies, revealing the Group 16 lone pair to be the definitive donor binding site and the dihalogen or interhalogen σ* orbital to be the most probable acceptor binding site (Fig. 1).[8,9] We therefore set out to experimentally prepare and characterise the first iodine monochloride thioether adducts and to use the structural information gained to verify the veracity of these previous calculations and to build a more accurate theoretical model for n-donor σ*-acceptor charge transfer adducts.

## Experimental section

NMR spectra were recorded on a Bruker DPX400 with TMS as an external standard. FT-Raman spectra were recorded in the range 500–50 $cm^{-1}$ on a LabRam Infinity microscopic laser Raman spectrometer, operating with a He/Ne laser (6328 Å) with a maximum power of 2 mW at sample. For all FT-Raman data the value in parentheses represent the relative intensities of the bands (strongest = 10). For reference the FT-Raman spectra of free dibenzyl sulfide was collected ($cm^{-1}$): 121(3.7), 134(2.9), 149(1.8), 164(1.5), 185(10), 306(1.5), 348(0.9), 466(3.6).

### Synthesis of $(PhCH_2)_2S\cdot ICl$ (1)

Iodine monochloride (0.38 g, 2.33 mmol) was added in small portions to a solution of dibenzyl sulfide (0.50 g, 2.33 mmol) in 8 ml of cyclohexane. The mixture was heated at reflux for 30 min and allowed to cool slowly overnight. The solid produced was isolated by filtration and washed thoroughly with hexane to yield small yellow needle-shaped crystals of **1** (yield 0.64 g, 78%). Anal: Calc. for **1**, $C_{14}H_{14}ClIS$: C 44.64, H 3.75; found C 44.89 H 3.67%. Mp 78–80 °C. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta = 4.05$ (s, 4H, $-CH_2-$), 7.25–7.32 (m, 10H, $-C_6H_5$). FT-Raman ($cm^{-1}$): 122(0.5), 135(1.5), 146(1.5), 158(1.3), 186(1.2), 196(2.1), 231(1.4), 255(10), 259(8.7), 313(0.8), 360(0.5), 467(0.2).

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† Electronic supplementary information (ESI) available: 3D coordinates in the form of MDL Molfiles and CML files, for all geometries and associated energies. See http://www.rsc.org/suppdata/nj/b4/b411873a/

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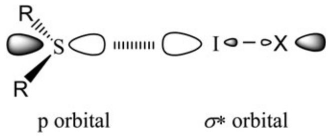

**Fig. 1** Schematic representation of a thioether n-donor, IX (X = Cl, Br, I) σ* acceptor charge transfer complex.

### Synthesis of $(PhCH_2)_2S\cdot IBr$ (2)

Iodine monobromide (0.48 g, 2.33 mmol) was added in small portions to a solution of dibenzyl sulfide (0.50 g, 2.33 mmol) in 15 ml of cyclohexane. The mixture was heated at reflux for 30 min and allowed to cool slowly overnight. The solid produced was isolated by filtration and washed thoroughly with hexane to yield small orange needle-shaped crystals of **2** (yield 0.78 g, 80%). Anal: Calc. for **2**, $C_{14}H_{14}BrIS$: C 39.93, H 3.35; found C 40.17 H 3.25%. Mp 68–70 °C. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 4.15 (s, 4H, $-CH_2-$), 7.28–7.48 (m, 10H, $-C_6H_5$). FT-Raman ($cm^{-1}$): 121(1.0), 138(3.1), 162(10), 172(8.0), 192(2.4), 209(2.1), 229(2.0), 295(0.3), 350(0.2), 459(0.3).

### X-Ray crystallography

Crystals of **1** and **2** suitable for X-ray diffraction were prepared *via* recrystallisation from toluene and were mounted directly on into the coldstream of an Oxford Cryostream crystal cooling apparatus, installed on either a Bruker P4/RA (**1**) or Bruker P4 (**2**) diffractometer, using perfluoropolyether oil. Essential crystallographic details are given in Table 1. Data were collected using the $\omega$–$\theta$ scan technique. Both structures were solvent by direct methods and refined based of $F^2$ using the SHELXTL and SHELX-97 program systems.[10] All atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. The absolute structures of both **1** and **2** were determined by a combination of $R$-factor tests [$R_1^+ = 0.0346$, $R_1^- = 0.0430$ for **1**; $R_1^+ = 0.0264$, $R_1^- = 0.0306$ for **2**] and by use of the Flack parameter [$x^+ = +0.00(3)$, $x^- = +1.00(3)$ for **1**; $x^+ = +0.00(4)$, $x^- = +1.00(4)$ for **2**]. CCDC reference numbers 225279, 225280. See http://www.rsc.org/suppdata/nj/b4/b411873a/ for crystallographic data in .cif or other electronic format.

**Table 1** Summary of crystal structure data for **1** and **2**

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{14}H_{14}ClIS$ | $C_{14}H_{14}BrIS$ |
| FW | 376.66 | 421.12 |
| Cryst. size/mm | 0.23 × 0.10 × 0.05 | 0.28 × 0.20 × 0.07 |
| Cryst. system | Monoclinic | Monoclinic |
| Space group | $P2_1$ (no. 4) | $P2_1$ (no. 4) |
| $a$/Å | 6.956(2) | 7.1678(6) |
| $b$/Å | 5.6659(10) | 5.7376(11) |
| $c$/Å | 18.636(5) | 18.5292(18) |
| $\beta$/° | 98.90(2) | 100.495(7) |
| $V$/Å$^3$ | 725.6(3) | 749.28(17) |
| $Z$ | 2 | 2 |
| $\lambda$/Å | 1.541 78 | 0.710 73 |
| $T$/K | 183(2) | 183(2) |
| $D_{calc}$/g cm$^{-3}$ | 1.724 | 1.867 |
| $\theta$ range/° | 2.40–62.93 | 2.24–25.00 |
| $\mu$/mm$^{-1}$ | 20.171 | 4.920 |
| No. of reflns. | 1420 | 1581 |
| No. of unique reflns. ($R_{int}$) | 1305 (0.0311) | 1460 (0.0276) |
| No. of params. | 143 | 143 |
| $R_1$ [$F_o^2 > 2\sigma(F_o^2)$]$^a$ | 0.0346 | 0.0264 |
| $wR_2$ (all data)$^b$ | 0.0843 | 0.0542 |
| Min/max electron residue/$e$ Å$^{-3}$ | +0.749/−0.857 | +0.568/−0.523 |

$^a$ $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$

### Computational details

Calculations were performed using the Gaussian 98 and Gaussian 03 programs,[11] using general basis sets[12] including the MIDI! basis set[13] and the pVTZ basis set.[14] The KMLYP method[15], CCSD method[16] and CPCM (polarizable conductor calculation model)[17] were used for the calculations. The KMLYP procedure[15] was invoked using the keywords iop(3/76 = 1000005570) iop(3/77 = 0000004430) and iop(3/78 = 0448010000) (Gaussian 03). Full geometry optimisation was followed by zero point and entropy energy correction using unscaled calculated frequencies. NBO analysis followed Weinhold's protocols.[18] All final coordinates and total energies are available *via* the electronic supplementary information.†

## Results and discussion

### Solid-state studies

Yellow needle shaped crystals of $(PhCH_2)_2S\cdot ICl$ **1** were obtained in high yield from a cyclohexane solution of iodine monochloride and dibenzyl sulfide. Crystallographic analysis revealed **1** to adopt the predicted spoke structure (Fig. 2, X = Cl) with a close to linear S–I–Cl arrangement [176.14(9)°] and S–I and I–Cl distances of 2.575(2) and 2.558(3) Å, respectively (Table 2). The S–I distance in **1** is therefore shorter than that in previously reported thioether IBr and $I_2$ adducts and this can be attributed to the increased acceptor ability of ICl. Although this is the first crystallographically characterised thioether ICl adduct, two other sulfur donor to ICl acceptor complexes have been reported in the literature; the ICl adducts of triphenylphosphine sulfide[11] and $N$-methylbenzothiazole-2(3$H$)-thione,[20] both containing close to linear S–I–Cl units and S–I distances of 2.641(1) and 2.556(1) Å, respectively (although in the later case there are also significant interactions between the Cl and the exo- and endo-cyclic sulfurs of two adjacent molecules). Note that in **1** there are no significant intermolecular interactions, with the shortest intermolecular approach to the chlorine atom being 3.65 Å from a hydrogen on the methylene carbon C(1) and the closest S···Cl contact being 3.78 Å.

We were also able to prepare and crystallographically characterise the IBr analogue of **1**, $(PhCH_2)_2S\cdot IBr$ **2**. Complex **2** is isostructural to **1** (Fig. 2, X = Br) with a S–I–Br angle of 174.81(5)° and S–I and I–Br distances of 2.6159(18) and 2.6896(10) Å, respectively (Table 2). The geometry of **2** is therefore directly comparable with previously reported thioether IBr adducts.[6] The shortest intermolecular approach to the bromine atom in **2** is 3.75 Å from a hydrogen on

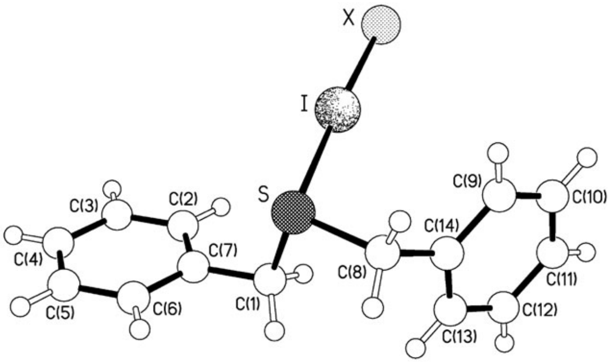

**Fig. 2** The molecular structure of $(PhCH_2)_2S\cdot ICl$ (**1**; X = Cl).

**Table 2** Selected bond lengths (Å) and angles (°) for $(PhCH_2)_2S \cdot IX$ complexes

| | X = Cl (**1**) | X = Br (**2**) | X = I[4] |
|---|---|---|---|
| I–X | 2.558(3) | 2.6896(10) | 2.819(9) |
| S–I | 2.575(2) | 2.6159(18) | 2.78(2) |
| C(1)–S | 1.817(9) | 1.836(8) | 1.82[a] |
| C(8)–S | 1.827(9) | 1.832(7) | 1.82[a] |
| S–I–X | 176.14(9) | 174.81(5) | 179[a] |
| C(1)–S–I | 99.8(3) | 99.5(3) | 100[a] |
| C(8)–S–I | 104.5(3) | 103.6(2) | 100[a] |
| C(1)–S–C(8) | 102.7(4) | 102.8(3) | 93[a] |

[a] ESDs not available.

the methylene carbon C(1), and the closest S···Br contact is 3.94 Å.

It is now possible to see that across the series $(PhCH_2)_2S \cdot IX$ [X = I,[4] Br (**2**), Cl (**1**)] there is a shortening of the S–I distance from 2.78(2) to 2.6159(18) to 2.575(2) Å as the acidic character of I–X increases from I to Br to Cl (Table 2). Concordantly the I–X bond is lengthened with respect to the gaseous I–X molecules as a certain amount of donor electronic charge is transferred to the antibonding σ* orbital of the IX molecule from the sulfur atom. The value of the I–X bond order ($n$) can be estimated using Pauling's equation:[21]

$$d(\text{I}-\text{X}) = d_o - 0.85\log(n)$$

where $d_o$ is the I–X bond length of IX in the gas phase ($d_o$ = 2.321, 2.469 or 2.666 Å for X = Cl, Br or I, respectively).[22] The I–X bond orders ($n$) for **1** and **2** are therefore 0.526 and 0.550 respectively, and $n = 0.660$ for the previously reported diiodide complex.[4] It has been stated by Bigoli *et al.* that neutral diiodide adducts can be classified into three classes according to the bond order ($n$) of the I–I bond: namely weak adducts with $n > 0.6$, strong adducts for $0.4 < n < 0.6$ and very strong adducts for $n < 0.4$.[23] Using this classification the diiodide complex $(PhCH_2)_2S \cdot I_2$ should be regarded as a weak adduct. Such a classification has also been extended using similar rules to IBr and ICl charge transfer complexes[19] and hence **1** and **2** should both be considered to be in the second class and therefore strong adducts.

Adduct formation between sulfur donors and IX species (X = I, Br, Cl) can also be observed experimentally using FT-Raman spectroscopy, whereby lengthening of the I–X bond results in a lowering of the $\nu$(I–X) stretching frequency (or more correctly in a lowering of the stretching frequency for the symmetric stretch of the S–I–X three bond system which has a major contribution from the $\nu$(I–X) vibration).[7,19] Hence, FT-Raman spectroscopy on **1** and **2** has been undertaken and reveals two significant new bands in both cases when compared to the spectra of uncomplexed dibenzyl sulfide (259 and 255 $cm^{-1}$ for **1** and 172 and 162 $cm^{-1}$ for **2**). Based on previous studies we are able to assign these bands as $\nu$(I–Cl) stretches in **1** and $\nu$(I–Br) stretches in **2**.[7,19] The presence of two distinct $\nu$(I–X) bands for both **1** and **2** instead of the expected one is most likely due to two different I–X environments in the crystal lattice. Previous studies on $I_2$ and IBr systems have revealed a close correlation between the FT-Raman data and adduct strength,[24] and the values obtained for $\nu$(I–X) in this work are consistent with the presence of strong adduct formation in both cases.[7,19]

Adduct formation in **1** and **2** was also observed to be quantitative in chloroform solution using $^1H$ NMR spectroscopy which showed a significant downfield shift of the dibenzyl sulfide methylene protons [$\delta$ = 4.05 (**1**); 4.15 (**2**) ppm *cf.* $\delta$ = 3.60 ppm for $(PhCH_2)_2S$].

## Theoretical studies

The large discrepancy (of up to 0.8 Å) between the observed bond distances in **1** and **2** with those previously calculated for $Et_2S \cdot IX$ (X = Cl, Br) using geometry optimization at the HF/3-21G*, HF/LANL2DZ and B3LYP/LANL2DZ levels,[8] prompted us to undertake new theoretical calculations on the model thioether system $Me_2S \cdot IX$ (X = F, Cl, Br, I). The electron rich character of these systems containing three adjacent heteroatoms bearing lone electron pairs suggests that both basis set and electron correlation effects are likely to dominate the errors. Previous calculations had employed relatively small basis sets, and so initially we investigated the larger all-electron triple-zeta basis[14] (Sadlej pVTZ). To enable a viable calculation with this size of basis (*e.g.*, 1018 primitive Gaussians for X = I) two density-functional based correlation treatments were selected for evaluation; the well established B3LYP hybrid[11] and the very recently reported KMLYP rehybridisation.[15] The latter is of particular interest since it has been suggested[25] that it might provide more accurate prediction of bond lengths for correlation-sensitive molecules. For this size of system, a periodic boundary calculation to estimate lattice effects on bond lengths is prohibitive, and so we approximated this using the CPCM polarizable conductor model.[17]

The results at the B3LYP/pVTZ level predict significantly better bond length agreement with the crystal structure values than previous calculations, although the error still tends towards a longer S–I (by around 0.35 Å) and a shorter I–X distance (Table 3) than the crystallographically observed distances in **1**, **2** and other previously reported $I_2$ [4,5] and I–Br[6] thioether adducts. We also included some other basis sets for comparison at this stage, focusing on the system with X = Cl for this comparison. The smaller 6-311G(d,p) triple-zeta basis predicts a slightly longer S–I bond, whilst the recently reported (and significantly smaller) MIDI! halogen set[13] actually shows slightly better agreement compared to pVTZ. This is perhaps not surprising, since the latter basis was not developed specifically for studying geometrical properties, unlike the MIDI! set. Overall however, these basis sets all predict an S–I distance of around 2.9 Å for X = Cl which is significantly larger than the crystallographically observed S–I distance of 2.575(2) Å in **1**.

We next investigated whether this remaining error might be due to the correlation treatment. Employing the KMLYP/pVTZ combination results in a further shortening of the predicted S–I bond distance (by up to 0.08 Å), although the I–X bond is now predicted to be too short by up to 0.19 Å (Table 3). Further improvement (or at least a more systematic approach) to the correlation model was sought in the CCSD (Coupled-Cluster with single and double excitations) method.[16] To enable such a calculation within the computational limits available to us, we restricted it to the 6-311G(d,p) and MIDI! basis sets. Compared to *e.g.* KMLYP, the CCSD level actually results in a predicted increase in the S–I bond distance of around 0.14 Å along with a slight contraction in the I–Cl distance, neither of which effect brings the calculations into closer agreement with the experimental structure. We therefore conclude that the remaining discrepancy is unlikely to be due to deficiencies in the electron correlation treatment alone.

Our final exploration involved two simple assessments of intermolecular and lattice effects on the geometry. The first approach was to investigate dimer formation. Moderately long intermolecular X···S (X = Cl, Br) distances were observed in the crystal structures of **1** and **2** (*vide supra*). Calculations on the $Me_2S \cdot ICl$ dimer using KMLYP/pVTZ confirm that these interactions appear to be relatively weak (<4 kcal $mol^{-1}$), with next to no effect on the computed S–I (2.805 Å) and I–Cl (2.397 Å) bond lengths. At the other extreme, modelling using the water continuum dielectric has a far greater effect, with the

**Table 3** Selected bond lengths (Å) and angles (°) for the complex $Me_2S \cdot IX$. Full coordinates and geometric information are available *via* the ESI

| X | Method | Total energy/a.u. | S–I/Å | I–X/Å |
|---|---|---|---|---|
| F | B3LYP/6-311G(d,p) | −7497.443 79 | 2.857 | 2.029 |
| F | B3LYP/pVTZ | −7498.368 88 | 2.796 | 2.014 |
| F | KMLYP/6-311G(d,p) | −7495.002 11 | 2.754 | 1.973 |
| F | KMLYP/pVTZ | −7495.953 01 | 2.713 | 1.948 |
| F | KMLYP(CPCM)/pVTZ[a] | −7495.955 73 | 2.592 | 2.019 |
| Cl | B3LYP/6-311G(d,p) | −7857.830 74 | 2.908 | 2.491 |
| Cl | B3LYP/pVTZ | −-7858.742 20 | 2.881 | 2.470 |
| Cl | KMLYP/6-311G(d,p) | −7855.162 16 | 2.827 | 2.410 |
| Cl | B3LYP/MIDI! | −7823.809 97 | 2.836 | 2.453 |
| Cl | KMLYP/MIDI! | −7821.184 82 | 2.778 | 2.377 |
| Cl | CCSD/6-311G(d,p) | −7853.948 15 | 3.047 | 2.428 |
| Cl | CCSD/MIDI! | −7819.682 86 | 2.971 | 2.388 |
| Cl | KMLYP/pVTZ | −7856.100 83 | 2.805 | 2.394 |
| Cl[b] | KMLYP/pVTZ | −15 712.2081 | 2.805 | 2.397, 3.715 |
| Cl | KMLYP(CPCM)/pVTZ[a] | −7856.101 01 | 2.623 | 2.493 |
| Cl | KMLYP(CPCM)/MIDI![a] | −7821.187 15 | 2.608 | 2.472 |
| Br | B3LYP/6-311G(d,p) | −9971.762 33 | 2.973 | 2.624 |
| Br | B3LYP/pVTZ | −9972.678 17 | 2.881 | 2.470 |
| Br | KMLYP/6-311G(d,p) | −9968.447 31 | 2.894 | 2.538 |
| Br | KMLYP/pVTZ | −9969.387 67 | 2.849 | 2.535 |
| Br | KMLYP(CPCM)/pVTZ[a] | −9969.387 02 | 2.648 | 2.634 |
| I | B3LYP/6-311G(d,p) | −14 317.152 97 | 3.059 | 2.824 |
| I | B3LYP/pVTZ | −14 318.981 71 | 3.025 | 2.807 |
| I | KMLYP/6-311G(d,p) | −14 313.162 45 | 2.996 | 2.729 |
| I | KMLYP/pVTZ | −14 315.032 79 | 2.962 | 2.715 |
| I | KMLYP(CPCM)/pVTZ[a] | −14 315.036 95 | 2.726 | 2.804 |

[a] Solvation model[17] at a permittivity of 80. [b] For the dimer $(Me_2S \cdot ICl)_2$.

KMLYP(CPCM)/pVTZ predicted bond lengths now relatively close (within 0.06 Å) to experimentally observed values, with this model both contracting the S–I distance and extending the I–X distance. This points to significant ionic character in these bonds and may provide at least a partial explanation of why gas phase computed geometries may not be entirely accurate models for such systems.

To explore the ionicity of these complexes, we first calculated the free energies of binding for the association of the $Me_2S \cdot IX$ adducts from the components $Me_2S$ and IX. The values (KYMYP/pTVZ) are $\Delta G^{298}{}_{\text{association}} = -0.2$ (X = I), −2.7 (X = Br), −3.9 (X = Cl) and −8.8 (X = F) kcal $mol^{-1}$ and therefore follow the anticipated trend, with the greatest binding energies occurring for the system containing the most electronegative halogen (X). These binding energies are also consistent with the modified Bigoli classification of **1**, **2** and $(PhCH_2)_2S \cdot I_2$ in the solid state (*vide supra*) with **1** and **2** both classified as strong adducts and hence with corresponding larger dissociation energies (3.9 and 2.7 kcal $mol^{-1}$, respectively) and $(PhCH_2)_2S \cdot I_2$ classified as a weak adduct and hence exhibiting a much lower dissociation energy (0.2 kcal $mol^{-1}$). On the basis of these calculations $(PhCH_2)_2S \cdot IF$ would be expected to be classified as a very strong adduct on the modified Bigoli scale.[19,23]

The bonding in these adducts was further examined using NBO analysis of orbital occupancies and corresponding perturbation energies (Table 4). In all cases charge transfer is observed from the lone pair on the sulfur (9.1% s, 90.7% p) to the vacant σ* orbital of the I–X acceptor. With increasing electronegativity of X this charge transfer increases in value with larger S to I–X interaction energies calculated and a corresponding lower sulfur lone pair occupancy and a higher I–X(σ*) occupancy. This interaction also leads to an increased positive charge on the sulfur and increased negative charge on the halogen X. The computed Wiberg bond index in the NAO basis indicates values of 0.72 and 0.30 for the I–Cl and I–S bonds, respectively in **1**, compared to the estimate of 0.53 for the former using the Pauling method; this discrepancy is probably due to the over-short predicted value for the I–Cl bond compared to the experimental values used for the Pauling method. The corresponding calculated I–X bond orders for X = F, Br and I of 0.50, 0.78 and 0.86 confirm the classification noted above. However, when the CPCM solvation model is applied, the Wiberg bond index for **1** changes from 0.72 and 0.30 to 0.58 and 0.47 for the I–Cl and I–S bonds, in much better agreement with the empirical Pauling estimates.

Vibrational analysis (of the gas phase models) also supports these bonding conclusions. The I–Cl stretch for the complex with $Me_2S$ (KMLYP/pVTZ) is reduced from 425 for free I–Cl to 346 $cm^{-1}$. Other modes are relatively unaffected (*e.g.* the C–S–C stretch reduces from 763 to 757 $cm^{-1}$ upon complexation; the C–S–C bend increases from 269 to 277 $cm^{-1}$) and a new mode is introduced (the S–I stretch) of 125 $cm^{-1}$. The corresponding reductions in I–F, I–Br and I–I stretches upon complexation are respectively 679 to 564, 295 to 242 and 242 to 204 $cm^{-1}$, whilst the S–I stretches progress as 154, (125), 113 and 97 $cm^{-1}$.

**Table 4** NBO analysis for the complex $Me_2S \cdot IX$ calculated at the (KMLYP)/pVTZ level

| Natural property | X = I | X = Br | X = Cl | X = F |
|---|---|---|---|---|
| Charge on X/a.u. | −0.15 | −0.30 | −0.41 | −0.66 |
| Charge on I/a.u. | −0.02 | +0.10 | +0.18 | +0.43 |
| $S_{lp}$ to I–X σ* Interaction energy/kcal $mol^{-1}$ | 30.8 | 45.7 | 50.5 | 63.5 |
| $S_{lp}$ occupancy/a.u. | 1.78 | 1.74 | 1.73 | 1.71 |
| X–I σ* occupancy/a.u. | 0.17 | 0.21 | 0.22 | 0.24 |

## Conclusion

In summary, two new thioether interhalogen adducts, (PhCH$_2$)$_2$S · ICl (**1**) and (PhCH2)$_2$S · IBr (**2**) have been prepared and crystallographically characterised. Although there has been much interest in the literature on the possible structures and applications of thioether interhalogen and dihalogen adducts, this is in fact the first reported example of a thioether I–Cl adduct. The 1 : 1 addition products between sulfur and dihalogens and interhalogens have been previously reported to exhibit much structural diversity, however in this case the solid-state structure of **1** is shown to be in keeping with previously reported R$_2$S diiodide and iodine monobromide adducts. Of particular interest are the observed S–I and I–Cl distances which differ considerably (by up to 0.8 Å!) from the recently theoretically predicted values for Et$_2$S · ICl.[8] This has led us to undertake a series of theoretical calculations on thioether (Me$_2$S) IX adducts (X = F, Cl, Br, I) which showed that the computed geometries for these systems, in particular the S–I and I–X distances, vary significantly based on the choice of basis set and type of density functional hybridisation model employed. In order to model these electron rich adducts accurately we have demonstrated the importance of using high quality basis sets and density functional hybridisation models which are able to handle electron correlation accurately and also the importance of lattice effects.

In conclusion, we consider that these electron rich complexes, where the geometries are likely to be unusually sensitive to correlation effects, may provide useful reference systems for evaluating different hybrid approaches for modelling highly correlated species.

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