DALTON

Evaluation of thermodynamic parameters for highly correlated chemical systems: a spectrophotometric study of the 1 : 1 and 2 : 1 equilibria between I_2 and 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione) (mbit) and 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione) (ebit). Crystal and molecular structures of mbit·2I_2 and ebit·2I_2

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The reactions of I_2 with 1,1′-methylene- and 1,1′-ethylene-bis(3-methyl-4-imidazoline-2-thione) (mbit and ebit) have been investigated in $CHCl_3$ solution at different temperatures by spectrophotometry. The experimental data have been processed using two different procedures of computer analysis: SUPERSPEC based on the conventional Gauss–Newton–Marquardt least-squares method; and POWELSPEC, based on Powell's direct search method for the refinement of ΔH° and ΔS°. The ability of the two methods to identify the involved equilibria correctly was compared. Evidence for the stepwise formation of the 1 : 1 and 1 : 2 adducts has been obtained by the two methods for the mbit case, while POWELSPEC only was able to solve the ebit case satisfactorily. The crystal structures of the adducts mbit·2I_2 and ebit·2I_2 have been determined. They show that the thionic sulfur atoms co-ordinate two diiodine molecules, with S–I 2.683(2) (mbit·2I_2) and 2.642(3) (ebit·2I_2) Å and with I–I 2.897(1) and 2.903(2) Å respectively, the two S–I–I groups being related by a two-fold axis. The structural features of the S–I–I linear group are in accordance with Fourier-transform IR and Raman spectral data and can be taken into account with a three-centre two-electron axial orbitally deficient bonding scheme.

We are extensively investigating the reactions of diiodine with molecules containing thioamido groups, both free[1] and co-ordinated to transition metals.[2] This includes synthetic work to prepare suitable donors D in order to try and obtain different products: neutral charge-transfer complexes,[3] oxidation products of the donor having polyiodides as counter ions,[4] and hopefully mixed-valence products.[5] Meanwhile solution and solid-state studies are also being carried out in order to clarify the nature of the diiodine–donor interaction. While D·I_2 molecular compounds are generally classified as being of the charge-transfer (c.t.) type, the increasing number of solution as well as solid-state studies on these systems has allowed three main types of adducts to be distinguished: D · · · I–I **1** D–I–I **2** and D–I · · · I **3**. In **1** long D · · · I and short I–I distances are found, while UV/VIS spectra show the well known c.t. band and the blue-shifted diiodine and donor bands, while one Raman peak due to the perturbed I_2 molecule is observed in the 180–140 cm^{-1} range.[6] In **2** the D–I and I–I distances are comparable, and correspond to a bond order of 0.5, which can be explained on the basis of a covalent three-centre two-electron bond. Accordingly UV as well as Raman features can be explained (presence of two peaks ascribable to the antisymmetric and symmetric stretching of D–I–I).[7] In **3**, where short D–I and long I · · · I distances are found,[8] the adduct may be envisaged as being due to the interaction of the donor I^- with the acceptor D–I^+. Only one peak ascribable to the D–I vibration is observed in the Raman spectrum. A very delicate balance between these forms exists in adducts at the borderlines, and in the solid-state weak interactions can stabilize a type of adduct different from that found in solution. In addition, an apparently insignificant modification of the molecular complexity of the donor in a class of molecules having the same donor group may produce unexpectedly different products.

In order to determine reliable equilibrium constants and related thermodynamic parameters for the donor–acceptor interaction it is very important to check that the procedures of computer analysis of the spectrophotometric data can correctly identify the equilibria involved. In fact such procedures, including the one used by SUPERSPEC (a computer program derived from SUPERQUAD[9]) and generally applied by us to calculate both molar absorption coefficients (ε) and equilibrium constants (β) simultaneously, are all based on the assumption that the following equation, derived from the well known Lambert–Beer law, is valid: $A = l\Sigma c_i \varepsilon_i = \Sigma f_i(\beta)\varepsilon_i$.† This equation is non-linear with respect to the parameters (β and ε_i); moreover it contains the product of these quantities. This introduces a strong correlation between the parameters to be determined and in some cases the least-squares minimization process may fail, as the matrix of the normal equations may be nearly singular. Such a correlation may be resolved if spectra of solutions containing the various absorbing species in a wide range of mutual molar ratios are available. If experimental reasons (solubility) do not allow the use of a wide range of reagent concentrations SUPERSPEC can fail. This happened in the case of the class of molecules A which bear two imidazoline-2-thione rings.[3] They react with diiodine to produce 1 : 2

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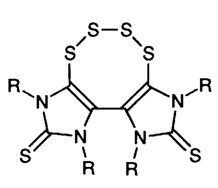
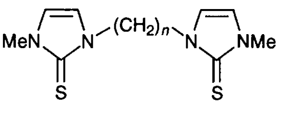
† A is the absorbance of the solution at a given wavelength, l the optical path length, c_i and ε_i the molar concentration and molar absorption coefficient (at the same wavelength) of the absorbing species and $c_i = f_i(\beta)$ a function of the equilibrium constant β.



A



$n = 1$, mbit; $n = 2$, ebit

molecular complexes which have been isolated in the solid state and characterized by X-ray diffractometric studies. In $CHCl_3$ solutions, however, only the 1 : 1 complex seemed to exist in the explored concentration range for R = Et and Ph, while in the R = Bu case a 1 : 2 complex could be observed.[10] We suspected that the chemical equivalence of the two thionic sulfurs involved in the co-ordination with I_2 could produce strongly correlated molar absorptions of the 1 : 1 and 1 : 2 species, thus introducing another source of correlation in SUPERSPEC. In these cases, the recently published computer program POWELSPEC[10] (based on Powell's direct search method[11]) which allows refinement of the standard enthalpy and entropy changes from a set of absorbance data at different temperatures, has been successfully used for the least-squares minimization of spectrophotometric data in accordance with the stepwise formation of 1 : 1 and 1 : 2 adducts.

In this paper we report results regarding the reaction of diiodine with the donors mbit = 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione) and ebit = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione) where, in analogy with the previously investigated systems, a high correlation between corresponding values of molar absorption and formation constants is expected to exist. The aims of the present study are: (*i*) to compare the ability of SUPERSPEC and POWELSPEC to characterize the equilibria involved; (*ii*) to compare the behaviour of these donors with those exhibited by the corresponding 2-selone derivatives, recently investigated by us,[7] which, in the corresponding case to mbit (*i.e.* mbis) gives rise to the 1 : 2 adduct, and in that corresponding to ebit (*i.e.* ebis) to a very uncommon hypervalent derivative with the chalcogen atom situated centrally between the iodine atoms; (*iii*) to compare the behaviour of these donors with that exhibited by 1,3-dimethylimidazoline-2-thione which with diiodine gives rise to two crystal modifications of a 1 : 1 adduct,[12] of the c.t type in accordance with its features in solution, while the bond distances in the solid state agree better with a three-centre two-electron covalent bond, D–I–I (**2**), description.

Results and Discussion

Solution studies

Two sets of solutions with a fixed donor concentration and varying diiodine concentrations in $CHCl_3$ were measured at six different temperatures in the range 10–35 °C. Typical examples of the spectra are shown in Fig. 1. The development of a strong band at 360 nm, the presence of two isosbestic points and the decrease in the donor band are clearly seen in both systems investigated. The spectrophotometric data have been analysed using the computer program SUPERSPEC, assuming that both complexes mbit·I_2 and mbit·$2I_2$ and ebit·I_2 and ebit·$2I_2$ are present at equilibrium. In the case of mbit, convergence is attained for all temperatures, the root-mean-square error on the absorbances being less than 0.01. The values of the formation constants of the complexes and those of the enthalpy and

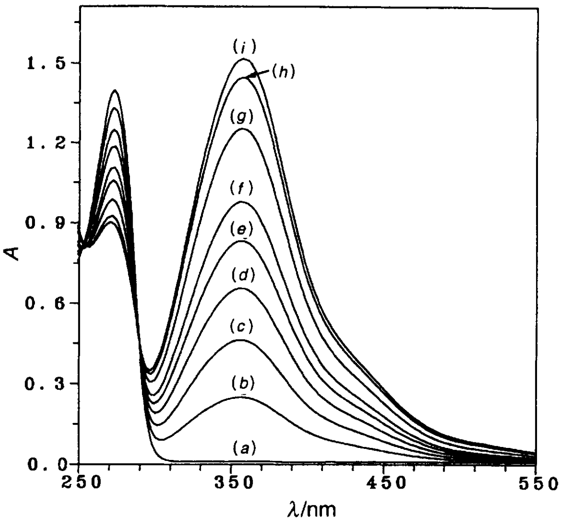


Fig. 1 The UV/VIS spectra at 293 K in an 0.1 cm silica cell of $CHCl_3$ solutions containing fixed amounts of mbit ($c = 5.0 \times 10^{-4}$ mol dm^{-3}) and variable I_2 concentrations in the ratios: (*a*) 1 : 0; (*b*) 1 : 0.2; (*c*) 1 : 0.4; (*d*) 1 : 0.6; (*e*) 1 : 0.8; (*f*) 1 : 1; (*g*) 1 : 1.4; (*h*) 1 : 1.8; (*i*) 1 : 2

entropy changes interpolated from the van't Hoff plot (correlation coefficients 0.999 and 0.991 for the 1 : 1 and 1 : 2 complexes respectively) are listed in Table 1. The same spectrophotometric data have been refined by the program POWELSPEC, recently described by us.[10] It uses Powell's direct minimization methods, and refines spectrophotometric data at all temperatures simultaneously, assuming; (*i*) that the equilibrium model is the stepwise formation of the 1 : 1 and 1 : 2 adducts; (*ii*) that the molar absorption coefficients are constant quantities within the investigated temperature range, and (*iii*) that the formation constants follow the van't Hoff equation. The ΔH° and ΔS° obtained are close enough to those obtained by SUPERSPEC (see Table 1). The differences, which are still significant in terms of the error limits of the parameters, are ascribed to the different assumptions of the two minimization methods. If the molar absorptions calculated by means of POWELSPEC are introduced as constant values in the SUPERSPEC refinement of the equilibrium constants, the resulting values do not differ significantly from those obtained using POWELSPEC.

By applying SUPERSPEC to the ebit + I_2 system convergence is attained only for temperatures below 30 °C. This failure is ascribed to the critical step of inversion of the normal equations matrix, which may be badly defined and nearly singular, when the parameters are highly correlated. On the contrary, Powell's method does not require inversion of any matrix for direct search for the minimum. In fact the same spectrophotometric data have been analysed successfully by means of POWELSPEC, and the refined values of the parameters are given in Table 2. It is noteworthy that the log β values obtained with SUPERSPEC at 20 and 25 °C are significantly different from those calculated with the POWELSPEC refinement parameters; moreover these values do not exhibit the expected decreasing trend with temperature. As a consequence, by comparing the performance of the two programs, we are confident that the POWELSPEC refinement provides the most reliable results. The values of the stepwise thermodynamic functions (log *K*, ΔH° and ΔS°) for the adduct formation at 25 °C are given in Table 3. It should be noted that the values of log *K* are very high, close to the generally accepted limit for the spectrophotometric determination of equilibrium constants.

The refined spectra (POWELSPEC) of the 1 : 1 and 1 : 2 complexes of I_2 with mbit are shown in Fig. 2. The corresponding spectra of the ebit adducts show similar features. The strong band at 360 nm is assigned to the c.t. transition,

Table 1 Logarithms of the equilibrium constants (standard deviations in parentheses) calculated by means of SUPERSPEC and POWELSPEC and standard enthalpy and entropy changes for the 1 : 1 (**1**) and 1 : 2 (**2**) complexes between mbit and I_2 in $CHCl_3$ solutions

	log β_1		log β_2	
T/°C	SUPERSPEC	POWELSPEC	SUPERSPEC	POWELSPEC
10	4.20(3)	4.1(1)	7.17(3)	7.07(7)
15	4.09(3)	4.0(1)	6.94(4)	6.82(7)
20	3.98(3)	3.9(1)	6.74(4)	6.58(6)
25	3.86(3)	3.35(2)	6.55(3)	6.35(6)
30	3.76(3)	3.25(2)	6.30(4)	6.13(6)
35	3.67(4)	3.14(2)	6.13(6)	5.91(6)
$\Delta H°$/kJ mol^{-1}	−35.6(8)	−36.4(4)	−70(1)	−77.8(4)
$\Delta S°$/J K^{-1} mol^{-1}	−46(3)	−50(2)	−109(4)	−138.9(8)

Table 2 Logarithms of the equilibrium constants (standard deviations in parentheses) calculated by means of SUPERSPEC and POWELSPEC and standard enthalpy and entropy changes for the 1 : 1 (**1**) and 1 : 2 (**2**) complexes between ebit and I_2 in $CHCl_3$ solutions

	log β_1		log β_2	
T/°C	SUPERSPEC	POWELSPEC	SUPERSPEC	POWELSPEC
10	4.78(6)	4.75(7)	8.7(1)	8.64(8)
15	4.69(4)	4.62(7)	8.5(1)	8.33(8)
20	4.62(4)	4.48(7)	8.32(8)	8.04(8)
25	4.75(7)	4.35(7)	8.5(1)	7.75(8)
30	n.c.[a]	4.23(7)	n.c.	7.47(8)
35	n.c.	4.10(7)	n.c.	7.20(8)
$\Delta H°$/kJ mol^{-1}	−43.26(8)[b]	−43.4(3)	−95.35(8)[b]	−95.9(3)
$\Delta S°$/J K^{-1} mol^{-1}	−61.84(8)[b]	−62(1)	−171.46(8)[b]	−173(1)

[a] n.c. = Not calculated: convergence was not obtained by applying SUPERSPEC to experimental data. However, by introducing the molar absorption coefficients calculated by means of POWELSPEC, convergence was attained for all temperatures, and the obtained β_1 and β_2 values were comparable, but with smaller standard deviations than those calculated by POWELSPEC. [b] Obtained *via* the van't Hoff equation using log β values calculated according to the procedure described in footnote *a*.

Table 3 Thermodynamic functions for the stepwise addition of diiodine to mbit and ebit at 25 °C in $CHCl_3$ solutions

Reaction	log K	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
$\text{mbit} + I_2 \rightleftharpoons \text{mbit}\cdot I_2$	3.8(1)	−36.4(4)	−50(2)
$\text{mbit}\cdot I_2 + I_2 \rightleftharpoons \text{mbit}\cdot 2I_2$	2.6(1)	−41.4(8)	−89(2)
$\text{ebit} + I_2 \rightleftharpoons \text{ebit}\cdot I_2$	4.35(7)	−43.4(3)	−62(1)
$\text{ebit}\cdot I_2 + I_2 \rightleftharpoons \text{ebit}\cdot 2I_2$	3.40(1)	−52.7(4)	−111(2)

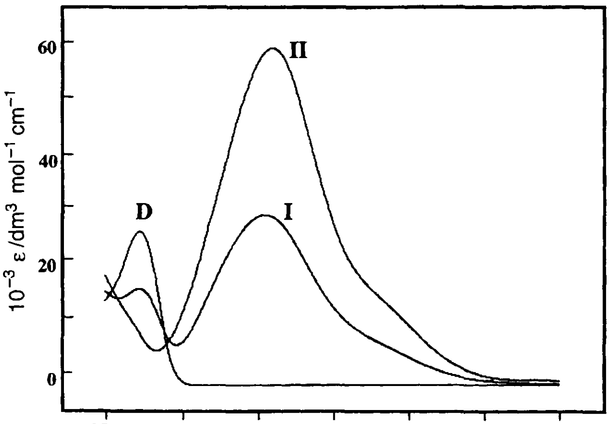


Fig. 2 Calculated UV/VIS spectra of the 1 : 1 (**I**) and 1 : 2 (**II**) complexes between mbit and I_2 at 283 K in $CHCl_3$ solutions. The spectrum of free mbit (D) is shown for comparison

while the shoulder near 430 nm is assigned to the diiodine blue-shifted band. These features are consistent with a description of the products as adducts of the c.t. type in solution. The values of $\Delta H°$ and $\Delta S°$ are comparable with those reported for donor–diiodine equilibria of similar strong thioamido S-donors.[10,13]

For the previously reported selenium (mbis) derivatives[7] the formation constants of the 1:1 and 1:2 adducts are much higher than those of mbit. Moreover the spectral features of these adducts are consistent with the formation of covalently bonded Se–I–I groups rather than c.t. adducts, as found in the mbit case. In the case of the corresponding ebis derivative the reaction with I_2 gives rise instead to a stable hypervalent 10–Se–3 compound (in which Se has ten electrons formally associated with it and three ligands bound to it) bearing I–Se–I groups.

Crystal and molecular structure of adducts mbit·2I$_2$ and ebit·2I$_2$

The molecules mbit·2I$_2$ and ebit·2I$_2$ lie on a two-fold axis (Figs. 3 and 4). The two ring moieties of ebit·2I$_2$ show a *gauche* conformation [N(1)–C(4)–C(4′)–N(1′) −73.4(10)°] as a consequence of the interactions determining the packing. The structural data for the organic molecules indicate that the aromatic bond systems (6π electrons) are almost completely delocalized in both compounds, as previously observed in similar thione[3,12] or selone[7] derivatives. The dihedral angle between the least-squares planes of the two approximately planar imidazoline rings is 99.2(2)° in mbit·2I$_2$, and that between the two planar imidazoline rings in ebit·2I$_2$ is 75.8(3)°. In both compounds the C–S–I–I moieties are not planar and the almost linear S–I–I fragments lie roughly perpendicular to the corresponding imidazoline ring owing to the substituents on the N atoms [torsion angles I–S–C–N in the range −96.4(4) to 84.4(4)° in mbit·2I$_2$ and −103.0(7) to 78.2(8)° in ebit·2I$_2$]. The contribution of sp^3 hybridization for S [C–S–I 96.8(1) for mbit·2I$_2$ and 98.2(3)° for ebit·2I$_2$] is very small. The orientation of the two S–I–I fragments [angles between the corresponding least-squares lines are 107.64(1) for mbit·2I$_2$ and 100.99(5)° for ebit·2I$_2$] is a consequence of intramolecular contacts involving the iodine atoms bonded to S atoms [4.059(2) for mbit·2I$_2$ and 4.292(2) Å for ebit·2I$_2$], so that these iodine atoms show a roughly T-shaped arrangement as observed in the previously

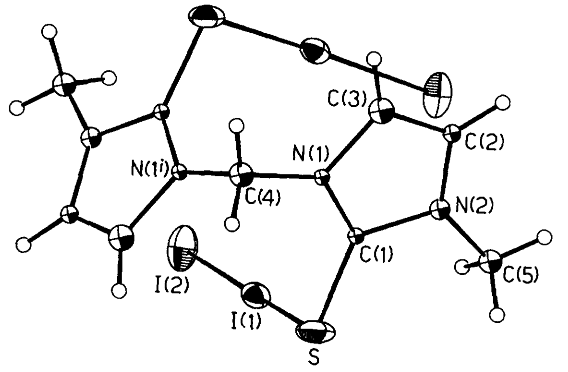


Fig. 3 Molecular structure and atom labelling scheme of the molecule mbit•2I$_2$. Selected bond lengths (Å) and angles (°): I(1)–I(2) 2.897(1), I(1)–S 2.683(2), S–C(1) 1.721(4), N(1)–C(1) 1.356(5), N(1)–C(3) 1.384(5), N(1)–C(4) 1.450(5), N(2)–C(1) 1.335(7), N(2)–C(2) 1.378(5), N(2)–C(5) 1.457(9), and C(2)–C(3) 1.326(9); I(2)–I(1)–S 175.71(3), I(1)–S–C(1) 96.8(1), and N(1)–C(4)–N(1$^{\text{i}}$) 112.5(2) (i $-x, y, \frac{1}{2} - z$)

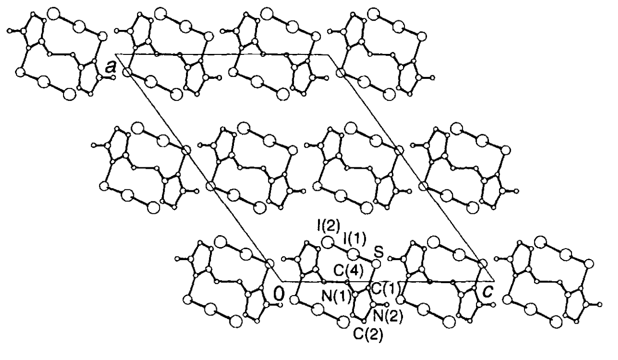


Fig. 4 Projection of the structure along [0 1 0] and atom labelling scheme of ebit•2I$_2$. Selected bond lengths (Å) and angles (°): I(1)–I(2) 2.903(2), I(1)–S 2.642(3), S–C(1) 1.703(6), N(1)–C(1) 1.35(1), N(1)–C(3) 1.38(1), N(1)–C(4) 1.45(1), N(2)–C(1) 1.33(1), N(2)–C(2) 1.35(1), N(2)–C(5) 1.45(2), C(2)–C(3) 1.35(2), and C(4)–C(4$^{\text{i}}$) 1.52(2); I(2)–I(1)–S 177.0(1) and I(1)–S–C(1) 98.2(3) (i $-x, y, \frac{1}{2} - z$)

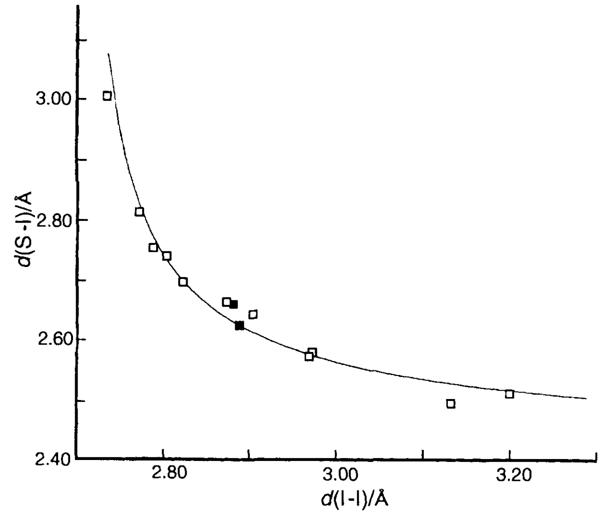


Fig. 5 Variation of d(S–I) with d(I–I) for thione–diiodine adducts reported in ref. 8 (□) and in this work (■)

mentioned selone adducts.[7] The weak interactions that are important in determining the packing are of the type I ··· C, S ··· C, C ··· C. The values of d(S–I) [2.683(2) for mbit•2I$_2$ and 2.642(3) Å for ebit•2I$_2$] and d(I–I) [2.897(1) for mbit•2I$_2$ and 2.903(2) Å for ebit•2I$_2$] are correlated, the lengthening of the intramolecular interaction being proportional to the shortening of the intermolecular interaction. This is a general phenomenon in molecular adducts. Bent[14] has found a hyperbolic curve fitting the experimental values of the two distances of linear triiodides. When d(I–I) is 2.92 Å the two interactions become indistinguishable and a bond order (according to Pauling[15]) of $n = 0.5$ can be calculated. Taking into account these distances and spectral features, a three-centre two-electron axially orbital-deficient bonding scheme has been proposed.[16] Other examples of hyperbolic correlation between the two distances in a linear triatomic fragment have been given by Bürgi,[17] and for the S–I–I case by Herbstein and Schwotzer.[8] The values of d(S–I) and d(I–I) for mbit•2I$_2$ and ebit•2I$_2$ fit this plot which is shown in Fig. 5. Moreover the I–I bond distances allow one to evaluate a bond order (I–I) near 0.5. A three-centre two-electron bonding scheme, analogous to that proposed for the triiodides and recently described for the Se–I–I group in 1,1′-methylenebis(3-methyl-4-imidazoline-2-selone),[7] can be conveniently used to describe the bonding in the triatomic S–I–I linear group. Accordingly these adducts should exhibit vibrational spectra different from those expected for c.t. adducts (type **1** adducts) and consistent with a covalently bonded S–I–I group (type **2** adducts) (see below). The adducts in the branches of the hyperbola with d(I–I) < 2.85, ($n \geqslant 0.6$) and > 3.01 Å ($n \leqslant 0.4$), can be assigned to type **1** and **3** respectively. At the borderlines between type **2** adducts and type **1** and **3** the spectroscopic features will help in understanding the nature of the interaction.

Vibrational spectroscopy

The solution Raman spectra of mbit and increasing amounts of I$_2$ show the presence of a single peak at 151 cm^{-1}, which grows on a weaker one due to the donor, up to the 1 : 2 (D : I$_2$) molar ratio. The position of this peak is in accordance with the expected shift of the frequency of unco-ordinated diiodine (ν 209 cm^{-1} in CHCl$_3$) upon co-ordination as a consequence of the lowering of the force constant of the I–I vibration in a c.t. adduct of type **1**.*[18] If the nature of the interaction between I$_2$ and the donor were the same in the solid adduct a single peak, expected to be so intense as to dominate the peaks of the donor, should appear nearly at the same position. The Fourier-transform Raman spectrum of the solid mbit•2I$_2$ instead exhibits different features and the more intense peaks appear in the range 200–100 cm^{-1} at 125 and 180–194 cm^{-1}. The comparison of this spectrum with that of a CHCl$_3$ solution of mbit and I$_2$ (in 1 : 2 molar ratio) is shown in Fig. 6. The IR spectrum below 200 cm^{-1} shows the presence of a peak at 125 and one at 180 cm^{-1}. The IR and Raman spectra of solid ebit•2I$_2$ (Fig. 7) show features similar to those of solid mbit•2I$_2$, while solution Raman spectra for ebit and I$_2$ mixtures could not be recorded since at the concentrations required to obtain satisfactory spectra the adduct precipitates. We tentatively assign the band at 120–125 cm^{-1} to the symmetric and the bands at 180–185 cm^{-1} to the antisymmetric stretching of the S–I–I group on the basis of their positions and relative intensities. The coincidence of these Raman and IR peaks can be explained by taking into account the high asymmetry of the system.† We can conclude that vibrational spectra[19] support the description of the solid adducts as three-centre two-electron covalently bonded D–I–I type **2** adducts in accordance with X-ray results, while in solution they appear as type **1** c.t. adducts, in accordance with UV/VIS spectroscopic results.

The other IR and Raman bands that are most significant in

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* This lowering is related to an increase in bond distance, in agreement with a molecular orbital description which shows that the highest occupied molecular orbital has some degree of σ^* I$_2$ antibonding character (see also ref. 6).

† In a symmetrical linear triatomic group the symmetric stretching is not infrared active but is Raman active, whereas the antisymmetric stretching is infrared active but not Raman active (see also ref. 7).

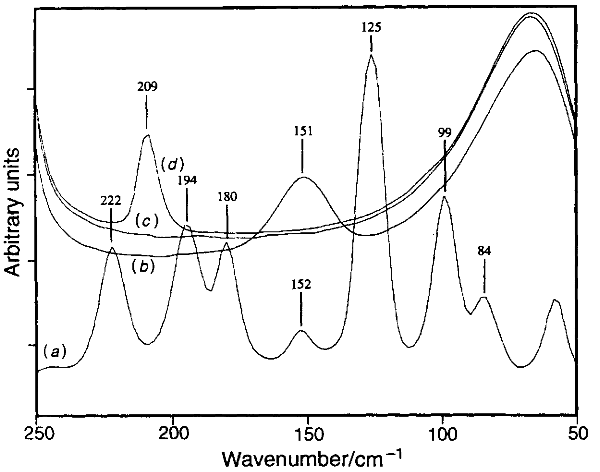

Fig. 6 Comparison of the Fourier-transform Raman spectrum of solid mbit·2I$_2$ (*a*) with that of mbit + I$_2$ (1:2) in CHCl$_3$ solution (*b*). The spectra of CHCl$_3$ (*c*) and of a CHCl$_3$ solution of I$_2$ (*d*, [I$_2$] = 0.10 mol dm^{-3}) are also displayed

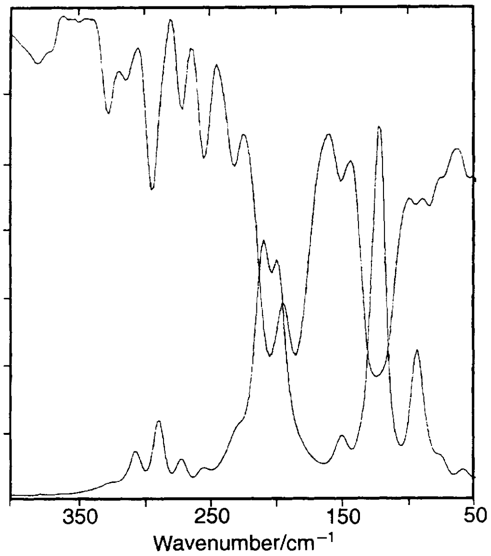

Fig. 7 Superimposed Fourier-transform Raman (lower) and IR (upper) spectra of ebit·2I$_2$ in the low-frequency region

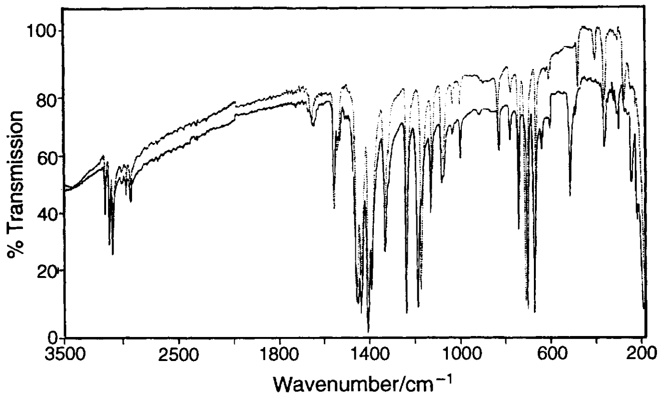

Fig. 8 Comparison of the Fourier-transform IR spectra of ebit (——) and ebis (. . .)

investigating the donor–acceptor interaction are the ν_{asym}(NCN) and ν(C=S) bands of the ligand. In fact sulfur donation should be accompanied by a shift to higher frequencies of ν_{asym}(NCN) and simultaneously to lower frequencies of ν(C=S). However the assignments of these bands in thioamides may be difficult since extensive coupling among vibrations may occur. Moreover the CS bond distance is significantly higher than in the double-bond (1.61 Å) case,[15] therefore the position of this band must be at significantly lower frequencies. This difficulty is shown by the differences found for the assignments given previously for the mbit and 1,3-dimethylimidazole-2-thione cases. For the latter Freeman *et al.*[12] assigned the band at 1560 cm^{-1} to ν(C=C), which upon complexation with I$_2$ is reported to undergo a positive shift to 1640 cm^{-1}. The bands at 1470 (free), 1490 (co-ordinated), and 1070, 730 (free), 1000, 820 cm^{-1} (co-ordinated) were assigned to the –N–C=S amide II and C=S vibrations respectively. In the mbit case Williams *et al.*[20] assigned the bands at 1580 and at 1175, 1160 cm^{-1} to ν_{asym}(NCN) and ν(C=S) vibrations respectively, even though they observed an 'enigmatic' direction of the shift of these bands upon complexation. In a recent reinvestigation of co-ordination-sensitive modes of 1,3-dimethylimidazole-2-thione, Williams *et al.*[21] compared the spectra obtained with those of the corresponding selenium-derivatives, following the so-called 'selenation' procedure. They found that the spectra were almost identical in the regions of the so-called thioamide modes except for the 1170–1180 cm^{-1} region. The bands found in this region were assigned to ν(C=S). Moreover significant differences were observed near 600 cm^{-1}. This in partial accordance with Jensen and Nielsen,[22] who rejected earlier the use of terms such as 'Amide II band', *etc.* recognizing that these bands often arise from the interaction among various vibrations, and that they do not have high C=S contributions since they are not significantly affected by the replacement of sulfur by selenium down to 900–800 cm^{-1}, in agreement with the predominant single-bond character of the CS vibration in thioamides. On the basis of a normal coordinate analysis, Dwarakanath and Sathyanarayana[23] have shown that the C=S vibration is distributed among other vibrations, and that its major contribution gives rise to a band at 516 cm^{-1} for imidazolidine-2-thione and at 357 cm^{-1} for imidazolidine-2-selone, in accordance with previous assignments by Devillanova and Verani.[24]

In order to find experimental support for the literature assignments we have compared the IR and Raman spectra of the free- and co-ordinated sulfur and selenium donors. Table 4 shows a summary of the results obtained and for further experimental evidence the spectra of the ebit and ebis cases are compared in Fig. 8. Our results are partially in disagreement with previous assignments of refs. 12, 20, and 21, while they agree with refs. 22–24. Regarding the assignments by Williams *et al.*,[20,21] the peak near 1570 cm^{-1} of the pro-ligand, which increases in intensity in the Raman spectrum and undergoes a small negative shift on co-ordination, can be assigned to ν(C=C) rather than to a ν_{asym}(NCN) vibration, which is expected to be more intense in the IR spectrum and to undergo a positive shift on co-ordination. The peaks near 1170 cm^{-1} undergo too small a shift on selenation to be due to the C=S vibration only. Regarding the assignments by Freeman *et al.*,[12] the band at 1470 cm^{-1} is almost unaffected by selenation, as previously observed by Williams *et al.*[20,21] This is ascribable to ν_{asym}(NCN) rather than to N–C=S vibration. Moreover, the peaks at 730–1070 cm^{-1} appear for both sulfur and selenium derivatives and therefore cannot be assigned to ν(C=S). Furthermore, the IR band at about 1560 cm^{-1} for the pro-ligand assigned to ν(C=C) is reported to undergo a shift to 1640 cm^{-1} on co-ordination. However, since co-ordination does not produce a shortening of the C=C bond and this band does not appear in the Raman spectrum, this assignment seems unlikely. This band may be an overtone of that at 820 cm^{-1}, or it may be related to the presence of traces of water in the sample.

The most significant shift is observed for a band falling near 520 cm^{-1}, which is found near 400 cm^{-1} for the selenium-derivative. Therefore this band seems to be related to a vibration with a higher C=S contribution in accordance with ref. 23. In conclusion, the most significant bands mainly related to the ν_{asym}(NCN) and ν(C=S) vibrations are found respectively near 1460 and 525–500 cm^{-1}.

Table 4 Selected IR (KBr pellets) and Raman peaks (cm^{-1}) of mbit, ebit and their diiodine adducts with tentative assignments. The peaks of the corresponding selenium derivatives mbis, mbis·$2I_2$ and ebis are also reported

	ν(C=C)		ν_{asym}(NCN)		Selenation-sensitive bands	
Compound	IR	Raman	IR	Raman	IR	Raman
mbit	1570m	1568vs	1464–1445vs	1468w, 1445m	1164s, 526s	1163vw, 550s
mbis	1567s	1568vs	1462–1448vs	1460 (sh)–1456mw	1128s, 396m	1117ms, 395s
mbit·$2I_2$	1563s	1562w	1476ms	1469w	1164–1155m, 526–507w	1160w, 525–505m
mbis·$2I_2$	1563s	1562w	1476vs	1473w	1135s, 383w	1139m, 382w
ebit	1566m	1564vs	1456–1444s	1481w	1194vs–1176 (sh), 1136mw, 517ms	1163–1152w, 539s
ebis	1559m	1561vs	1456–1442vs	1463mw (br)	1175vs, 1126m, 404mw	1133ms, 412ms
ebit·$2I_2$	1558s	1561w	1473s	1477w	1194s, 1157s, 524w	1190m, 1158w, 496s

Conclusion

The present study has shown that: (*i*) the computer program POWELSPEC is more powerful in evaluating thermodynamic parameters of highly correlated systems than SUPERSPEC and other programs based on similar procedures; (*ii*) the interaction of diiodine with mbit and ebit gives rise to molecular compounds which show features typical of type **1** c.t. adducts in solution, and of type **2** adducts in the solid state; thus their behaviour is different from that shown by mbis and ebis; (*iii*) vibrational spectroscopy in the low-frequency region is highly diagnostic in distinguishing the different types of adducts in accordance with X-ray structural data; and (*iv*) the most significant band related to the ν(C=S) vibration is found near 520 cm^{-1}, as shown by selenation experiments.

Experimental

Materials

Reagents and solvents of reagent-grade quality were used as furnished by Aldrich. The mbit donor was prepared according to ref. 25. The ebit compound was obtained as white needles (65% yield) with the same procedure described for mbit but using 1,1′-ethylenebis(3-methylimidazolium) diiodide (10 g, 0.02 mol) as the starting material. Thin-layer chromatographic analysis showed that this compound is homogeneous.

ebit. M.p. 215 °C (Found: C, 42.1; H, 5.4; N, 21.9; S, 25.1. $C_{10}H_{14}N_4S_2$ requires C, 42.2; H, 5.55; N, 22.0; S, 25.2%. IR (cm^{-1}): 3160w, 3126mw, 3096mw, 2975vw, 2938vw, 1566m, 1548w, 1536w, 1456s, 1444s, 1414vs, 1396s, 1337vs, 1244vs, 1194vs, 1176 (sh), 1136mw, 1089mw, 1044vw, 1007w, 834w, 783w, 746s, 706vs, 676s, 641w, 606vw, 517ms, 491w, 364m, 305mw, 251m, 192mw and 80m (br). Raman (cm^{-1}): 3157m, 3122mw, 3092m, 2986w, 2927ms (br), 1564vs, 1481w, 1450w (br), 1438s, 1402s, 1341m, 1327m, 1163w, 1152w, 1090w, 1042mw, 832vw, 813mw, 689mw, 666m, 604mw, 539s, 475w, 315w, 281mw, 245mw, 177mw and 131m.

The compounds mbit·$2I_2$ and ebit·$2I_2$ were prepared by allowing to stand at 4 °C CH_2Cl_2 solutions of the pro-ligands and I_2 in 1 : 2 molar ratio. After several days lustrous red-brown crystals suitable for X-ray diffraction studies were obtained.

mbit·$2I_2$. IR (cm^{-1}): 3156m, 3127mw, 3107w, 1563s, 1476ms, 1469ms, 1430ms, 1391s, 1389w, 1369m, 1332m, 1318m, 1262s, 1226s, 1205m, 1164m, 1155m, 1143vs, 1089mw, 1072mw, 1020w, 961w, 834ms, 796s, 766s, 729vs, 683m, 666ms, 649w, 604mw, 526w, 507w, 467mw, 294m, 243w, 217ms, 181ms, 152w and 125s (br). Raman (cm^{-1}): 3157w, 3129w, 3102w, 2980w, 2935w, 1562w, 1469w, 1428mw, 1419mw, 1390m, 1365mw, 1333w, 1260w, 1200w, 1160w, 1087w, 1018w, 959w, 793w, 729w, 683mw, 667mw, 649w, 602w, 525m, 505m, 288m, 261w, 222ms, 194ms, 180ms, 152w, 125vs, 99ms and 84 (sh) (Found: C, 14.6; H, 1.5; N, 7.9; S, 8.7. $C_9H_{12}I_4N_4S_2$ requires C, 14.45; H, 1.6; N, 7.5; S, 8.6%).

ebit·$2I_2$. IR (cm^{-1}): 3159w, 3123w, 3099w, 1558s, 1473s, 1435ms, 1392m, 1369w, 1332w, 1270ms, 1237m, 1228ms, 1194s, 1157s, 1086mw, 1050w, 948w, 936m, 832ms, 730vs, 677s, 669ms, 651mw, 524w, 327w, 294w, 271w, 254w, 231w, 205s, 185s, 151vw, 124s, 94vw and 74vw. Raman (cm^{-1}): 2941m, 1561w, 1477w, 1438mw, 1406vs, 1393s, 1369vs, 1333w, 1269m, 1236w, 1190m, 1158w, 1086w, 731mw, 679m, 650ms, 627w, 600w, 522w, 496s, 306m, 288s, 271m, 254w, 209vs, 199vs, 150w, 121vs, 93s and 59w (Found: C, 15.5; H, 1.7; N, 7.2; S, 8.4. $C_{10}H_{14}I_4N_4S_2$ requires C, 15.8; H, 1.85; N, 7.35; S, 8.4%).

Spectroscopic measurements

IR. Spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer model 983 spectrophotometer as KBr pellets; the far-Fourier-transform spectra (400–50 cm^{-1}) were obtained on a Bruker IFS55 spectrometer working at room pressure and using a flux of dried air.

Fourier-transform Raman. Spectra (resolution ± 4 cm^{-1}) were recorded on a Bruker RFS100 FTR spectrometer, fitted with an indium–gallium arsenide detector (room temperature) and operating with an excitation frequency of 1064 nm (Nd: YAG laser). The power level of the laser source was 300 mW for the solution samples, 100 mW for the pro-ligands and varied between 20 and 40 mW for the products. The $CHCl_3$ solutions and the solid samples, in the form of powders (mbit and ebit) or crystals (mbit·$2I_2$ and ebit·$2I_2$), were introduced into a suitable cell (Suprasil 300, Hellma cell of 0.5 cm thickness) and into a capillary tube respectively, and then fitted into the compartment designed for a 180° scattering geometry. No sample decomposition was observed during the experiments.

Three solutions with fixed concentration of mbit (1.5×10^{-2} mol dm^{-3}) and increasing concentrations of I_2 in the ratios 1 : 0.5, 1 : 1, and 1 : 2 were prepared. Owing to the different solubilities of the mbit·$2I_2$ and ebit·$2I_2$ adducts, the spectra of the $CHCl_3$ solutions of ebit and diiodine were not recorded.

UV/VIS. Electronic spectra were recorded in $CHCl_3$ solutions with a Cary 5 spectrophotometer equipped with a temperature-probe accessory connected to a thermostattable multi-cell block.

mbit. Two sets of solutions containing a fixed concentration of mbit [(*a*) 5.0×10^{-4}, (*b*) 1.0×10^{-4} mol dm^{-3}) and variable I_2 concentrations ranging from; (*a*) 1.00×10^{-4} to 1.00×10^{-3} mol dm^{-3} (ratios [mbit] : [I_2] = 1 : 0.2, 1 : 0.4, 1 : 0.6, 1 : 0.8, 1 : 1, 1 : 1.4, 1 : 1.8, and 1 : 2; see Fig. 1) and (*b*) 4.0×10^{-4} to 4.0×10^{-3} mol dm^{-3} (ratios [mbit] : [I_2] = 1 : 4, 1 : 8, 1 : 12, 1 : 20 and 1 : 40) were prepared and their spectra measured at six different temperatures (10–35 °C) in the range 250–550 nm, in 0.1 cm silica cells.

ebit. Two sets of solutions containing a fixed ebit concentration [(*a*) 1.5×10^{-5}, (*b*) 2.5×10^{-5} mol dm^{-3}] and variable I_2 concentrations ranging from (*a*) 3.0×10^{-6} to 3.0×10^{-4} mol dm^{-3} (ratios [ebit] : [I_2] 1 : 0.2, 1 : 0.4, 1 : 0.6, 1 : 0.8, 1 : 1, 1 : 1.4, 1 : 1.6, 1 : 2, 1 : 3.04, 1 : 4, 1 : 5.04, 1 : 8, 1 : 12 and 1 : 20) and (*b*) 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} (ratios [ebit] : [I$_2$] 1 : 4, 1 : 8, 1 : 12, 1 : 20, 1 : 30 and 1 : 40) were prepared and their spectra measured at six different temperatures as for mbit.

Calculations

In the case of mbit, the previously described program SUPERSPEC,[1] derived from SUPERQUAD,[9] was used to refine the equilibrium constants β_i and the molar absorptions ε_i simultaneously from the experimental absorbances, taken every 10 nm in the range 250–550 nm at six different temperatures in the range 10–35 °C. The total number of experimental points was 3317. The values of ΔH° and ΔS° were calculated by least-squares fitting of the corresponding ln β *versus* $1/T$ according to the van't Hoff equation. The same experimental data were used to calculate ΔH°, ΔS° and the molar absorptions by POWELSPEC.[10] The assumption was made that ε_i do not vary in the explored temperature range. In the case of ebit only POWELSPEC was used to refine ΔH°, ΔS° and ε_i. The total number of experimental points was 3720.

Crystallography

Crystal data for mbit·2I$_2$. $C_9H_{12}I_4N_4S_2$, $M_r = 747.96$, monoclinic, space group *C*2/*c*, $a = 18.643(6)$, $b = 9.324(5)$, $c = 13.494(5)$ Å, $\beta = 125.97(2)°$, $U = 1898(1)$ Å^3, $Z = 4$, $D_c = 2.617$ Mg m^{-3}, $F(000) = 1352$, μ(Mo-Kα) = 67.79 cm^{-1}, crystal dimensions $0.13 \times 0.15 \times 0.30$ mm.

Crystal data for ebit·2I$_2$. $C_{10}H_{14}I_4N_4S_2$, $M_r = 761.99$, monoclinic, space group *C*2/*c*, $a = 18.575(5)$, $b = 9.486(6)$, $c = 13.978(7)$ Å, $\beta = 125.99(2)°$, $U = 1993(2)$ Å^3, $Z = 4$, $D_c = 2.540$ Mg m^{-3}, $F(000) = 1384$, μ(Mo-Kα) = 64.60 cm^{-1}, crystal dimensions $0.29 \times 0.48 \times 0.55$ mm.

Diffraction measurements were made on a Philips PW 1100 diffractometer for mbit·2I$_2$ and on a Enraf-Nonius CAD4 diffractometer for ebit·2I$_2$, at room temperature using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å): θ–2θ scan mode, $3.0 < \theta < 27.0°$, 3006 reflections measured, 1829 observed [$I \geqslant 2\sigma(I)$] for mbit·2I$_2$; ω–2θ scan mode, $3.0 < \theta < 30.0°$, 3002 reflections measured and 1829 observed [$I \geqslant 2\sigma(I)$] for ebit·2I$_2$. Intensity data were corrected for Lorentz-polarization effects, and an empirical absorption correction was made by measuring two reflections with a χ value near 90° at different ψ values (0–180°, in steps of 10°) for mbit·2I$_2$, and following Walker and Stuart[26] using the program ABSORB[27] for ebit·2I$_2$ (minimum and maximum transmission factors 0.70890, 1.29926). Structure solution was by the Patterson method of SHELXS 86;[28] refinement by full-matrix least squares using SHELX 76,[29] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of mbit·2I$_2$ were placed at their geometrically calculated positions (C–H 0.96 Å) and refined by 'riding' on the corresponding carbon atoms; those of ebit·2I$_2$ were clearly located in the final ΔF map and refined isotropically. Final refinement (on *F*) resulted in $R = 0.0298$, $R' = 0.0473$, reflections/parameters ratio 20.78, residual electron density -1.60, 0.73 e Å^{-3} for mbit·2I$_2$: $R = 0.0505$, $R' = 0.0681$, reflections/parameters ratio 17.31, residual electron density -2.30, 1.49 e Å^{-3} for ebit·2I$_2$. Weighting scheme employed: $w = 1/[\sigma^2(F_o) + gF_o^2]$ with $g = 0.006822$ for mbit·21$_2$ and 0.014843 for ebit·2I$_2$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/169.

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