Kinetic and Mechanistic Study of the Reaction between Dithiomalonamides and Diiodine. Crystal Structure of the Compounds 3,5-Bis(ethylamino)-1,2-dithiolylium Triiodide and 3,5-Bis(morpholino)-1,2-dithiolylium Iodide Monohydrate

Roberto Ambrosetti,[a] Giuseppe Bellucci,[b] Roberto Bianchini,[b] Francesco Bigoli,[c] Paola Deplano,*[d] Maria Angela Pellinghelli[c] and Emanuele F. Trogu[d]
[a] *Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, Via Risorgimento 35, I-56126 Pisa, Italy*
[b] *Dipartimento di Chimica Bioorganica dell'Universita', Via Bonanno 33, I-56126 Pisa, Italy*
[c] *Istituto di Chimica Generale ed Inorganica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*
[d] *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche dell'Universita', Via Ospedale 72, I-09124 Cagliari, Italy*

The reaction of *N,N'*-diethyldithiomalonamide with I_2 has been investigated spectrophotometrically. A kinetic study carried out with the stopped-flow technique has shown the transient formation of a 1:1 *N,N'*-diethyldithiomalonamide·I_2 charge-transfer complex having a formation constant K_1 = 2.3(3) × 10^3 dm^3 mol^{-1} at 25 °C. This is followed by an oxidation–reduction reaction leading to 3,5-bis(ethylamino)-1,2-dithiolylium iodide and HI_n (n = 1 or 3), through a first- and a second-order process with respective rate constants at 25 °C k_1 = 0.84(7) s^{-1} and k_2 = 2.0(3) × 10^3 dm^3 mol^{-1} s^{-1}, consisting of an unassisted or I_2 assisted heterolytic fission of the I–I bond as the slow step. Further associative equilibria of 3,5-bis(ethylamino)-1,2-dithiolylium iodide and HI with free I_2 leading to the corresponding triiodides have also been observed, having formation constants, respectively, K_2 = 6.2(7) × 10^5 dm^3 mol^{-1} and K_3 = 8.9(5) × 10^6 dm^3 mol^{-1}. All the kinetic and thermodynamic parameters were obtained by an expressly devised computational method based on nonlinear least-squares procedures. An X-ray crystal structure analysis of the title compounds, obtained as products of the reaction between I_2 and $RNR'C(S)CH_2C(S)R'NR$, showed that the crystals obtained in the RNR' = EtNH and I_2 excess case are monoclinic, space group *C*2/*m*, with *a* = 13.643(6), *b* = 9.749(5), *c* = 11.879(6) Å, β = 99.76(2)° and *Z* = 4. The structure consists of chains running parallel to [010], where the 3,5-bis(ethylamino)-1,2-dithiolylium cations and triiodide anions are connected through two strong interactions involving the terminal iodide atom of the unsymmetrical I_3^- ($I_2 \cdots I^-$ anion) and both the sulphur atoms of the disulphide group. In the RNR' = OC_4H_8N and 1:1 reagents ratio case the crystals are monoclinic, space group $P2_1/c$, with *a* = 9.256(4), *b* = 20.257(6), *c* = 8.483(4) Å, β = 90.91(2)° and *Z* = 4. The structure consists of layers, approximately parallel to (201), determined by contacts involving $[OC_4H_8NC(S)CHC(S)NC_4H_8O]$ cations, iodide anions and water molecules.

A renewed interest is currently devoted to the charge-transfer (CT) complexes of diiodine with selected donors, including those of sulphur containing molecules, which have also been used to synthesize organic CT conductors[1] and antithyroid drugs.[2]

In recent studies on these reactions, in particular we have used donors containing one or more thioamido groups, both free[3–5] and coordinated to transition metals.[6–9] The formation of CT complexes was always observed, the site of interaction with I_2 being always the thiocarbonyl sulphur, even when several electron donor sites were available in the molecule (IR and X-ray evidence). In several cases these CT complexes are inert in solution and can be isolated in the solid state (see for example the $R_2NC(S)C(S)NR_2$[4] and the $RNC(S)N(R)C{=}CSSSSC{=}CN(R)C(S)NR$[5] cases), while in other cases the CT complex further evolves to give oxidation–reduction products [see for example the $R_2NC(S)SSC(S)NR_2$ case in which the donor is oxidised to a trithiolane cation[3]].

As an extension of this work, we decided to examine the behaviour of the I_2–dithiomalonamide $[RR'NC(S)CH_2C(S)NRR']$ system. It has been known for a long time that I_2 oxidizes dithiomalonamides to 3,5-diamino-1,2-dithiolylium cations,[10] the latter being used in the dye industry.[11] Although several papers concerning the synthesis and properties of these compounds have been published,[12,13] to our knowledge the mechanism of the above reaction has not yet been studied. In this paper we now report the results of a spectrokinetic investigation of the reaction of I_2 with *N,N'*-diethyldithiomalonamide $[(EtNH)_2dtm]$ to give 3,5-bis(ethylamino)-1,2-dithiolylium iodide $[(EtNH)_2dtlI]$, that has allowed us to clarify the reaction mechanism. The X-ray structures of the title compounds are also reported, in order to show the sulphur–iodine interactions associated with the cation–anion disposition.

Experimental

Preparation of the Compounds.—*N,N'*-diethyldithiomalonamide $[(EtNH)_2dtm]$ was prepared according to a literature method, by reacting diethylmalonate with aqueous ethylamine and then treating the resulting *N,N'*-diethylmalonamide in refluxing toluene with Lawesson's reagent.[14]

Bis(morpholyl)dithiomalonamide (mo_2dtm) was prepared by reacting malonyl dichloride with morpholine (1:4 ratio) in $CHCl_3$. After elimination of the precipitated morpholine hydrochloride, followed by a water extraction of the excess reagent, the dimorpholylmalonamide obtained was refluxed in

Table 1 Experimental data for the crystallographic analyses

Compound	[EtNHC(S)CHC(S)NHEt]I_3	[$OC_4H_8NC(S)CHC(S)NC_4H_8O$]I·$H_2O$
Formula	$C_7H_{13}I_3N_2S_2$	$C_{11}H_{19}IN_2O_3S_2$
M_r	570.027	418.307
Crystal system	monoclinic	monoclinic
Space group	*C*2/*m*	*P*2$_1$/*c*
a/Å	13.643(6)	9.256(4)
b/Å	9.749(5)	20.257(6)
c/Å	11.879(6)	8.483(4)
β/°	99.76(2)	90.91(2)
V/Å^3	1557(1)	1590(1)
Z	4	4
D_c/Mg m^{-3}	2.432	1.747
F(000)	1040	832
Temperature/K	295	295
Crystal size/mm	0.19 × 0.29 × 0.30	0.16 × 0.29 × 0.69
Diffractometer	Siemens AED	Siemens AED
μ(MoKα)/cm^{-1}	61.93	22.48
Scan type	θ/2θ	θ/2θ
Scan speed/° min^{-1}	2.5–12	2.5–12
Scan width/°	1.10 + 0.346 tanθ	1.10 + 0.346 tanθ
Radiation	Nb-filtered MoKα ($\bar{\lambda}$ = 0.710 73 Å)	
θ-Range	2.5–27	3.0–27
Reflections for lattice parameters number	27	28
θ-range	11–16	10–16
Standard reflection measured after every 50	1 5–4	2 7 2
Data collected	*h*,*k*, ± *l*	±*h*,*k*,*l*
No. of reflections measured	1822	3511
Condition for observation	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
No. of reflections used in the refinement	1097	1878
No. of refined parameters	97	107
R^a (Rw^a)	5.19 (6.49)	7.34 (11.34)
GOF^a	0.61	0.98
k,g ($w = k/\sigma^2(F_o) + gF_o^2$)	1.0 0.008 232	0.8547 0.008 556
Min/max height in final Δρ (e Å^{-3})	−1.32/1.46	−0.91/1.26

[a] $R = [\Sigma||F_0| - |F_c||]/\Sigma|F_0|$; $Rw = [(\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2]^{\frac{1}{2}}$; $\mathrm{GOF} = [(\Sigma w||F_0| - |F_c||)^2/(N_{\mathrm{data}} - N_{\mathrm{params}})]$.

toluene for 4 h with a slight excess of Lawesson's reagent. The final products were recovered in almost quantitative yield, by evaporation of toluene and recrystallized from ligroine.

3,5-βis(alkylamino)-1,2-dithiolyl iodides and triiodides [(RR′N)$_2$dtl]I_n (n = 1 or 3); dithiomalonamides and I_2 were mixed in halogenated solvents in different ratios ranging from a ligand excess to a diiodine excess. By slow concentration of these solutions, crystals of the mono- or tri-iodides (depending on the ratios of the reagents), respectively, separated as white or red–brown solids.

Elemental analyses are in accordance with the following formulations:

(EtNH)$_2$dtlI (Found: C, 26.2; H, 4.1; N, 8.3. Calc. for $C_7H_{13}N_2S_2I$: C, 26.59; H, 4.14; N, 8.86%).

(EtNH)$_2$dtlI$_3$ (Found: C, 15.0; H, 2.5; N, 5.1. Calc. for $C_7H_{13}N_2S_2I_3$: C, 14.75; H, 2.30; N, 4.91%).

mo$_2$dtlI·H_2O (Found: C, 31.3; H, 4.9; N, 6.8. Calc. for $C_{11}H_{19}N_2S_2O_3I$: C, 31.58; H, 4.58; N, 6.70%).

mo$_2$dtlI$_3$·H_2O (Found: C, 19.6; H, 2.9; N, 4.1. Calc. for $C_{11}H_{19}N_2S_2O_3I_3$: C, 19.66; H, 2.85; N, 4.17%).

Conductance measurements of the above derivatives were obtained in nitromethane by using a WTW-LBR type conductance bridge. Λ_{eq} fell in the 80–90 ohm^{-1} cm^2 range at 25 °C for solutions 1.0 × 10^{-3} mol dm^{-3}. These values are consistent with a 1 : 1 electrolyte formulation.

X-Ray Analysis.—The relevant data concerning the crystal structure analyses are summarized in Table 1. The final accurate values of the cell parameters were determined by least-squares refinement against 27 and 28 reflections for 3,5-bis(ethylamino)-1,2-dithiolylium triiodide [(EtNH)$_2$dtlI$_3$] and 3,5-bis(morpholino)-1,2-dithiolylium iodide monohydrate (mo$_2$dtlI·H_2O), respectively. The data were corrected for Lorentz and polarization effects; no absorption correction was applied. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares methods using anisotropic thermal parameters for all the non-hydrogen atoms in (EtNH)$_2$dtlI$_3$, anisotropic thermal parameters for iodine and the ring atoms and isotropic parameters for all the other non-hydrogen atoms in mo$_2$dtlI·H_2O, because of very poor crystals. The hydrogen atoms in (EtNH)$_2$dtlI$_3$ were located from a Δ*F* map and their coordinates were introduced in the final structure factor calculation; the coordinates of methylene- and dithiolyl-H atoms in mo$_2$dtlI·H_2O, placed at their geometrically calculated positions, were introduced in the final structure factor calculation as fixed contributors. Scattering factors, with corrections for anomalous dispersion, were taken from International Tables.[15] All calculations were performed on the CYBER 76 computer of CINECA (Casalecchio, Bologna) with financial support from the University of Parma, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma) using the SHELX-76 system of computer programs[16] and the programs PARST,[17] PLUTO[18] and ORTEP.[19] Table 2 gives the final atomic coordinates; selected bond distances and angles are in Table 3. The crystallographic numbering scheme and the ORTEP drawing of the cation are shown in Figs. 1 and 2 for (EtNH)$_2$dtlI$_3$ and mo$_2$dtlI·H_2O, respectively. Fractional atomic

Table 2 Fractional atomic coordinates (× 10^4)

	x/a	y/b	z/c		x/a	y/b	z/c
(a) $[EtNHC(S)CHC(S)NHEt]I_3$							
I(1)	1977(1)	5000	−5658(1)	C(1)	424(6)	3778(9)	1566(7)
I(2)	2670(1)	5000	−3353(1)	C(2)	−15(8)	5000	1814(10)
I(3)	3365(1)	5000	−693(1)	C(3)	−770(7)	2228(9)	2246(9)
S	1474(2)	3942(3)	944(2)	C(4)	−502(10)	2212(17)	3520(11)
N	85(5)	2548(8)	1699(6)				
(b) $[OC_4H_8NC(S)CHC(S)NC_4H_8O]I\cdot H_2O$							
I	8079(1)	3993(0)	3548(1)	C(3)	3795(10)	2522(5)	1302(14)
S(1)	5094(3)	3082(1)	1954(4)	C(4)	5016(14)	538(7)	2306(16)
S(2)	6494(3)	2379(1)	2764(4)	C(5)	5827(20)	−48(9)	2172(22)
O(1)	6801(10)	−136(5)	3482(12)	C(6)	7786(20)	397(11)	3520(21)
O(2)	97(11)	3262(5)	−761(13)	C(7)	7238(18)	1015(8)	3553(19)
O(3w)	1517(13)	699(6)	721(15)	C(8)	2484(13)	3460(6)	239(15)
N(1)	5861(10)	1122(4)	2583(11)	C(9)	1028(15)	3706(7)	67(17)
N(2)	2546(9)	2767(4)	726(11)	C(10)	65(16)	2653(7)	52(18)
C(1)	5423(10)	1710(5)	2204(13)	C(11)	1441(12)	2335(6)	71(14)
C(2)	4093(11)	1865(5)	1473(14)				

Table 3 Selected bond distances/Å and angles/° with esds in parentheses[a]

Bond	Length	Bond	Angle
(a) $[EtNHC(S)CHC(S)NHEt]I_3$			
I(1)–I(2)	2.741(2)	I(1)–I(2)–I(3)	177.43(8)
I(2)–I(3)	3.141(2)	S(′)–S–C(1)	95.3(3)
S–S(′)	2.063(4)	S–C(1)–C(2)	115.5(5)
S–C(1)	1.727(9)	C(1)–C(2)–C(1′)	118.4(5)
C(1)–C(2)	1.39(1)	S–C(1)–N	118.3(7)
C(1)–N	1.30(1)	C(2)–C(1)–N	126.1(8)
N–C(3)	1.46(1)	C(1)–N–C(3)	125.2(8)
C(3)–C(4)	1.50(2)	N–C(3)–C(4)	112.1(9)
(b) $[OC_4H_8NC(S)CHC(S)NC_4H_8O]I\cdot H_2O$			
S(1)–S(2)	2.037(4)	C(3)–S(1)–S(2)	94.8(4)
S(1)–C(3)	1.74(1)	S(1)–S(2)–C(1)	95.5(3)
S(2)–C(1)	1.74(1)	S(2)–C(1)–C(2)	116.0(8)
C(1)–C(2)	1.41(1)	C(1)–C(2)–C(3)	116.0(9)
C(2)–C(3)	1.37(1)	C(2)–C(3)–S(1)	117.7(8)
C(1)–N(1)	1.30(1)	S(2)–C(1)–N(1)	118.2(8)
C(3)–N(2)	1.34(1)	C(2)–C(1)–N(1)	125.7(9)
—	—	C(1)–N(1)–C(4)	123.3(9)
—	—	C(1)–N(1)–C(7)	121.4(10)
—	—	C(4)–N(1)–C(7)	114.9(10)
—	—	S(1)–C(3)–N(2)	117.5(7)
—	—	C(2)–C(3)–N(2)	124.7(9)
—	—	C(3)–N(2)–C(8)	119.1(9)
—	—	C(3)–N(2)–C(11)	121.0(9)
—	—	C(8)–N(2)–C(11)	116.5(9)

[a] Key to asymmetry operations (′): $x, 1 - y, z$.

coordinates for the H-atoms of $mo_2dtlI\cdot H_2O$, complete tables of bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Spectrokinetic Measurements.—Weighed quantities of bisublimed I_2 (C. Erba RPE >99.9%) were dissolved in 1,2-dichloroethane (C. Erba RPE >99.5%) purified as previously reported.[20] UV–VIS spectra were obtained on a Pye Unicam SP8-400 UV–VIS spectrophotometer and exhibited an excellent stability for at least 2 h, the average time interval for a kinetic measurements session. The molar absorptivity of I_2 in 1,2-dichloroethane solution at the monitored wavelength λ = 430 nm (ε = 150 dm^3 mol^{-1} cm^{-1}) was found to be constant and reproducible, and no trace of contaminant I_3^- (ε = 3.6 × 10^3 dm^3 mol^{-1} cm^{-1} at λ = 430 nm) was detected.

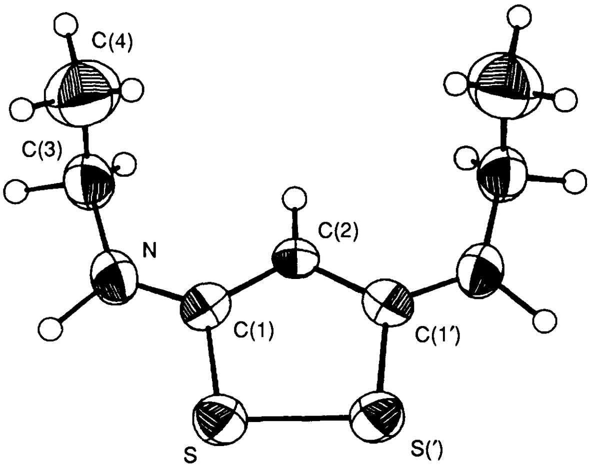


Fig. 1 ORTEP drawing of $(EtNH)_2dtlI_3$ showing thermal ellipsoids at 50% probability

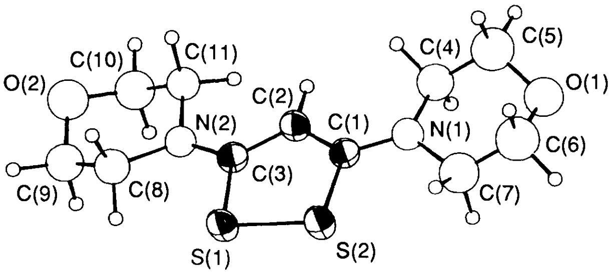


Fig. 2 ORTEP drawing of mo_2dtlI showing thermal ellipsoids at 50% probability

Equal volumes of $(EtNH)_2dtm$ and I_2 solutions were mixed in a Durrum Model D-110 stopped-flow apparatus equipped with a 2 cm observation cell and a data acquisition system able to record the absorbances of reaction mixtures at time intervals down to a minimum of 100 μs.[21] Temperature control of the

---

* For details of the CCDC deposition Scheme see 'Instructions for Authors (1991),' *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

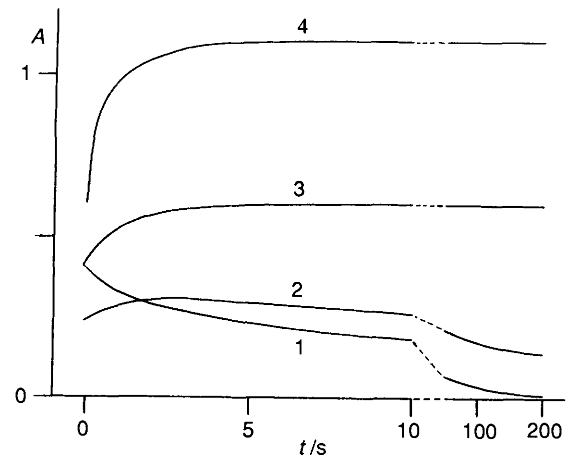


Fig. 3 Absorbance at λ = 430 nm *versus* time for 1,2-dichloroethane solutions of $(EtNH)_2dtm$ and I_2 at 25 °C at several reagent ratios: $[(EtNH)_2dtm]/[I_2] = 79$ (curve 1); 8 (2); 2.4×10^{-2} (3); 4.0×10^{-2} (4)

reagent solution (± 0.05 °C) was achieved with a Lauda MK70 constant temperature circulating bath.

Equilibrium Measurements.—Three sets of 1,2-dichloroethane solutions of constant $(EtNH)_2dtlI$ concentration (5.0×10^{-6}, 1.0×10^{-5} and 2.0×10^{-5} mol dm^{-3}) and diiodine concentrations ranging from a 1:1 to 20:1 excess with respect to $(EtNH)_2dtlI$ (22 solutions were used) were prepared and the electronic spectra recorded between λ = 270 and 340 nm in 1.0 cm cells at 25 °C, using a Varian model 2300 spectrophotometer equipped with an automatic system of data acquisition (DS 15) and with a Lauda K2RD thermostat (± 0.1 °C).

Computational Procedures.—The fit of the absorbance/concentration data required a non-linear least squares procedure because of the intrinsic non-linearity of the mathematical relation between the measured quantities.[22–24] This program was obtained by combining that developed for the multiple equilibria established between an alkene and bromine[25] with the one employed for dealing with the many reaction paths exhibited by the cyclohexene–Py•Br_2 system.[26]

All results reported in this paper were obtained using a constant-weight scheme for residuals, computed in absorbance units. This is justified in practice by the small spectrophotometric error, which alone would require[24] constant weights on the absorbance scale, with respect to the one presumably arising from non-exactly known initial concentrations. Fittings with constant weights on the absorbance scale were also done, yielding very similar results. The sum of the squared residuals divided by the number of degrees of freedom (variance of the fit) will be quoted as s_0^2 and its square root (r.m.s. standard deviation of the fit) as s_0.

The computational procedure for the case concerning the formation of a 1:1 and 1:2 complex of the donor (D) to I_2 is described.

Conservation of mass requires eqns. (*a*) and (*b*) to be fulfilled,

$$[D]_{tot} = [D] + [D{\cdot}I_2] + [D{\cdot}2I_2] \qquad (a)$$

$$[I_2]_{tot} = [I_2] + [D{\cdot}I_2] + 2[D{\cdot}2I_2] \qquad (b)$$

where $[D]_{tot}$ and $[I_2]_{tot}$ are the total reagent concentrations. Expressing the concentrations of the two complexes as a function of [D] and of $[I_2]$ through the formation constants for the 1:1 and 1:2 complexes (K_1 and K_2), a set of two equations in two unknowns ([D] and $[I_2]$) is obtained, as in eqns. (*c*) and (*d*).

$$[D]_{tot} = [D] + K_1[D][I_2] + K_2[D][I_2]^2 \qquad (c)$$

$$[I_2]_{tot} = [I_2] + K_1[D][I_2] + 2\,K_2[D][I_2]^2 \qquad (d)$$

Whilst multiple solutions of the problem exist in mathematical terms, chemical intuition indicates that a unique set of equilibrium concentrations holds. Furthermore, each reagent's equilibrium concentration is bound to be positive and less than the total value of that reagent, as in eqns. (*e*) and (*f*).

$$0 < [D] < [D]_{tot} \qquad (e)$$

$$0 < [I_2] < [I_2]_{tot} \qquad (f)$$

As a consequence, if we look at eqns. (*c*) and (*d*) as expressions relating [D] to $[I_2]$, and plot *e.g.* [D] *vs.* $[I_2]$, the two curves so obtained must have a unique crossing point within the rectangle limited by the conditions (*e*) and (*f*). This crossing point, representing the unique set of chemically acceptable equilibrium concentrations, was found by an iterative numerical procedure.

Since the complexes formed are reactive, the non-linear fitting program dealing with reaction kinetics had to take into account both equilibrium and kinetic processes. This was obtained by employing a specialized[27] numerical integration of the set of differential equations describing the reaction kinetics: at each integration step the resulting concentrations were brought back to equilibrium by repeating the procedure illustrated above.

The least-squares analysis was carried out using the 'normal equations' procedure.[22,24] This gives, as a necessary 'by-product', the variance-covariance matrix of the parameters. The square root of its *i*-th diagonal element gives the estimate of the standard deviation on the *i*-th fitting parameter (given in the text within parentheses after the parameter value), while the ratio between the *i,j*-th off-diagonal element and the square root of the product of the *i*-th and *j*-th diagonal elements gives the total correlation coefficient between the *i*-th and *j*-th parameters (quoted in the text as *r*). The estimate of the standard deviation is affected considerably by the non-linearity of the model, although in an unpredictable way. The usual 95% interval confidence limit for the parameters should be therefore increased to at least three times the standard deviation quoted in the following Tables.[22] All computations were carried out on AT compatible PC.

Results

When solutions of I_2 and $(R_2N)_2dtm$ in 1,2-dichloroethane were mixed at room temperature the appearance and the electronic spectrum of the mixture changed relatively quickly. The behaviour of the two $(R_2N)_2dtm$ compounds investigated was similar, but since we have made a complete study in solution only in the $(EtNH)_2dtm$ case, from now on we refer only to this last derivative.

Initial absorbances higher than expected on the basis of the free reagent's contribution were measured at λ = 430 nm immediately after mixing 1,2-dichloroethane I_2 and $(EtNH)_2dtm$ solutions using the stopped-flow instrument. Depending on the initial concentrations of the reagents, different reaction behaviour was observed (Fig. 3). In the presence of a large excess of $(EtNH)_2dtm$ to diiodine a regular decay of the initial absorbance was observed (curve 1); with a lower excess of the initial $(EtNH)_2dtm$ an absorbance maximum arose, followed by a slow decay (curve 2); when a large I_2 excess relative to $(EtNH)_2dtm$ was used a fast increase of the initial absorbance

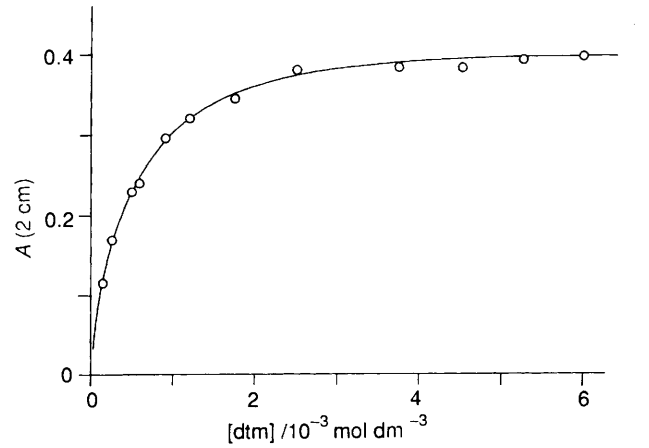


Fig. 4 Plot of initial absorbances at λ = 430 nm and 25 °C *versus* [$(EtNH)_2dtm$] for runs 1–12 of Table 4

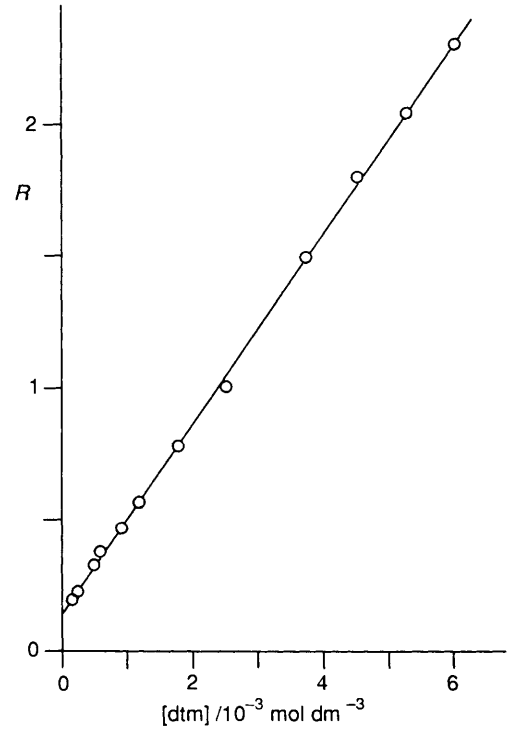


Fig. 5 Plot of R = [$(EtNH)_2dtm$] × [I_2] × A_0^{-1} *versus* [$(EtNH)_2dtm$] for runs 1–12 of Table 4

up to a constant value (curves 3 and 4) was found. In the last case the final UV-VIS spectrum was consistent with the presence, besides unreacted I_2, of triiodide species at a concentration twice that of the initial $(EtNH)_2dtm$. These species were formed through the equilibrium reaction of the free I_2 with dithiolylium iodide and with HI [Scheme 1, eqns. (4) and (5)].

At least three different equilibria appeared to be involved: one leading to the initially formed high-absorbing species [eqn. (1) of Scheme 1], and the other two described in eqns. (4) and (5). Moreover, a reaction that in principle could obey a single or two different kinetic laws, producing $(EtNH)_2dtlI$ and HI_n (n = 1 or 3), was involved.

$$(EtNH)_2dtm + I_2 \overset{K_1}{\rightleftharpoons} (EtNH)_2dtm{\cdot}I_2 \qquad (1)$$

$$(EtNH)_2dtm2{\cdot}I_2 \xrightarrow{k_1} (EtNH)_2dtlI + HI \qquad (2)$$

$$(EtNH)_2dtm{\cdot}I_2 + I_2 \xrightarrow{k_2} (EtNH)_2dtlI + HI_3 \qquad (3)$$

$$(EtNH)_2dtlI + I_2 \overset{K_2}{\rightleftharpoons} (EtNH)_2dtlI_3 \qquad (4)$$

$$HI + I_2 \overset{K_3}{\rightleftharpoons} HI_3 \qquad (5)$$

Scheme 1

In order to simplify the treatment of this complex reaction scheme, involving several equilibria and reaction kinetics, we first tried to obtain the values of K_1, K_2 and K_3 separately.

Equilibrium Measurements.—The initial absorbance values A_0, measured at λ = 430 nm immediately after mixing equal volumes of 1,2-dichloroethane I_2 and $(EtNH)_2dtm$ solutions in a stopped flow apparatus, are reported in Table 4. Runs 1–12 show that at constant [I_2] = 7.6 × 10^{-5} mol dm^{-3}, A_0 values higher than expected on the basis of the negligible contribution of the free I_2, and rising A_0 values with increasing [$(EtNH)_2dtm$], were found. Fig. 4 gives a plot of A_0 values *versus* [$(EtNH)_2dtm$] for these runs. A complete complexation of the halogen was obtained above [$(EtNH)_2dtm$] = 3 × 10^{-3} mol dm^{-3}. Assuming that only a 1:1 complex was present under the conditions of runs 1–12 of Table 1, a molar extinction coefficient value of $\varepsilon = 2.6 \times 10^3$ dm^3 mol^{-1} cm^{-1} could be evaluated from the data in Fig. 4. An estimate of the formation constant $K_1 = 2.57 \times 10^3$ mol dm^{-3} and of the molar absorptivity of the complex, $\varepsilon_{430} = 2.78 \times 10^3$ dm^3 mol^{-1} cm^{-1}, were obtained by fitting the A_0 values to the Scott equation for 1:1 complexes (Fig. 5).[21]

In order to rule out the existence of higher-order equilibria, these estimates were used as starting parameters in a non-linear least-squares fitting procedure (NLLSQ) of all initial absorbance data of Table 4. The contribution of the free I_2 to A_0 was negligible in runs 1–12, but substantial in runs 13–20 (60–80% of the overall A_0). Assuming a 1:1 stoichiometry for the $(EtNH)_2dtm{\cdot}I_2$ complex, an excellent fitting was obtained with the following formation constant and molar absorptivity values: $K_1 = 2.3(3) \times 10^3$ dm^3 mol^{-1}, $\varepsilon = 2.8(1) \times 10^3$ dm^3 mol^{-1} cm^{-1}. Individual K_1 and ε values were well defined, as shown by their satisfactory low correlation coefficient ($r = -0.805$). Moreover, the general goodness of the fit was confirmed from the very low value obtained for the parameter $s_0 = 0.015$, representing the square root of the variance of the fitting in percent absorbance units. No evidence for a further 1:2 CT complex between $(EtNH)_2dtm$ and I_2 was obtained from the present data, the inclusion of such a complex only leading to a divergence of the fitting procedure.

Equilibrium (4) was investigated spectrophotometrically in the λ = 275–330 nm range for mixtures of (1 × 10^{-5})–(5 × 10^{-4}) mol dm^{-3} I_2 and of (5 × 10^{-6})–(2 × 10^{-5}) mol dm^{-3} $(EtNH)_2dtlI$ in 1,2-dichloroethane at 25 °C. The iodide salt exhibited a stable UV absorption band (λ_{max} = 305 nm, $\varepsilon_{max} = 2.55 \times 10^4$ dm^3 mol^{-1} cm^{-1}), which, in the presence of increasing amounts of I_2, underwent a hyperchromic and ipsochromic shift to λ = 300 nm, due to the formation of the corresponding triiodide salt. Spectrophotometric measurements [251 experimental points taken from 22 solutions of $(EtNH)_2dtlI$ and I_2] were used in a NLLSQ fitting procedure to obtain the following formation constant for the equilibrium (4): $K_2 = 6.2(7) \times 10^5$ dm^3 mol^{-1}. The calculated absorption curve in the investigated λ = 275–330 nm range for $(EtNH)_2dtlI_3$ is reported in Fig. 6, together with the spectrum of the iodide salt. The goodness of the fit was proved by the s_0 = 0.018 value.

The high absorption of $(EtNH)_2dtlI$ at λ = 305 nm ($\varepsilon = 2.55 \times 10^4$ dm^3 mol^{-1} cm^{-1}) is explained, as in the case of the

Table 4 Stoichiometric concentrations, initial absorbances at λ = 430 nm and best-fit parameters for the reaction of I_2 and *N*,*N*′- diethyldithiomalonamide (dtm) in 1,2-dichloroethane at 25 °C[a]

Run	$[I_2]$/ mol dm^{-3}	[dtm]/ mol dm^{-3}	A_o[b] (2 cm cell)	[dtm]/$[I_2]$	[CTC][c]/ mol dm^{-3}	$K_3/10^6$ dm^3 mol^{-1}	k_1/s^{-1}	$k_2/10^3$ dm^3 mol^{-1} s^{-1}
1*a*	7.6×10^{-5}	6.00×10^{-3}	0.396	79	7.1×10^{-5}	8.14(19)	0.79(1)	0
1*b*						8.34(29)	0.78(1)	2.00
2	7.6×10^{-5}	5.26×10^{-3}	0.392	69	7.0×10^{-5}	9.77(24)	0.90(1)	2.00
3	7.6×10^{-5}	4.51×10^{-3}	0.382	59	7.0×10^{-5}	9.42(25)	0.92(1)	2.00
4*a*	7.6×10^{-5}	3.74×10^{-3}	0.382	49	6.8×10^{-5}	8.93	0	2.8×10^2 (2.3×10^1)
4*b*						9.52(24)	0.90(1)	2.00
5*a*	7.6×10^{-5}	2.50×10^{-3}	0.380	33	6.5×10^{-5}	9.42(27)	0.96(3)	0
5*b*						8.69(19)	0.95(2)	2.00
6	7.6×10^{-5}	1.75×10^{-3}	0.345	23	6.1×10^{-5}	8.95(18)	0.90(3)	2.00
7*a*	7.6×10^{-5}	1.20×10^{-3}	0.320	16	5.6×10^{-5}	8.38(1.81)	0.94(5)	0
7*b*						8.71(22)	0.85(4)	2.00
8	7.6×10^{-5}	9.0×10^{-4}	0.296	12	5.1×10^{-5}	8.40(35)	0.80(4)	2.00
9*a*	7.6×10^{-5}	6.0×10^{-4}	0.240	8	4.4×10^{-5}	8.35(19)	0.80(5)	0
9*b*						8.25(13)	0.79(8)	2.00
10	7.6×10^{-5}	5.0×10^{-4}	0.230	6.5	4.0×10^{-5}	9.40(23)	0.75(4)	2.00
11	7.6×10^{-5}	2.5×10^{-4}	0.170	3.3	2.7×10^{-5}	8.75(33)	0.79(4)	2.00
12	7.6×10^{-5}	1.5×10^{-4}	0.115	2	1.8×10^{-5}	8.99(99)	0.77(2)	2.00
13	3.76×10^{-4}	2.5×10^{-5}	0.163	6.5×10^{-2}	1.2×10^{-5}	8.93	0.84	2.13(0.27)
14	5.00×10^{-4}	2.5×10^{-5}	0.216	5.0×10^{-2}	1.4×10^{-5}	8.93	0.84	1.96(0.14)
15	6.27×10^{-4}	2.5×10^{-5}	0.254	4.0×10^{-2}	1.5×10^{-5}	8.93	0.84	2.09(0.37)
16	7.52×10^{-4}	2.5×10^{-5}	0.315	3.3×10^{-2}	1.6×10^{-5}	8.93	0.84	1.72(0.13)
17*a*	8.78×10^{-4}	2.5×10^{-5}	0.381	2.8×10^{-2}	1.7×10^{-5}	8.93	0	0.77(0.62)
17*b*						8.93	0.84	2.53(0.20)
18*a*	1.01×10^{-3}	1.2×10^{-5}	0.376	1.2×10^{-2}	8.9×10^{-6}	8.93	3.30(20)	0
18*b*						8.93	0.84	1.92(0.11)
19*a*	1.01×10^{-3}	2.5×10^{-5}	0.404	2.4×10^{-2}	1.8×10^{-5}	8.93	1.04(21)	0
19*b*						8.93	0.84	1.58(0.15)
20*a*	1.26×10^{-3}	5.0×10^{-5}	0.619	4.0×10^{-2}	3.7×10^{-5}	8.93	0	3.69(0.95)
20*b*						8.93	3.04(10)	0
20*c*						8.93	0.84	2.08(0.14)

[a] Values without standard deviations are given as fixed parameters. [b] Initial absorbances measured immediately after mixing at λ = 430 nm. At this wavelength *N*,*N*′-diethyldithiomalonamide does not absorb and ε_{I_2} = 150 dm^3 mol^{-1} cm^{-1}. [c] Calculated equilibrium concentration immediately after mixing.

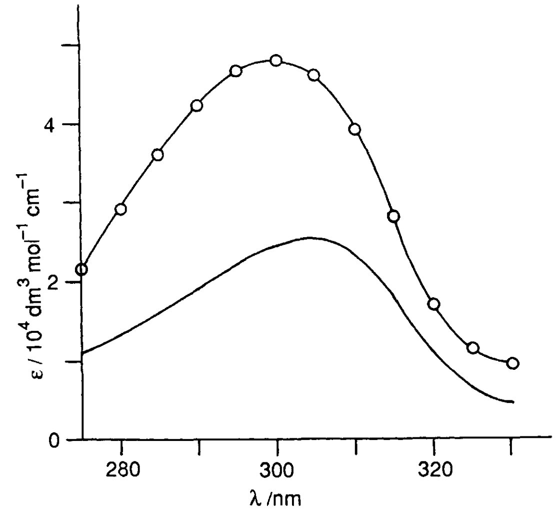


Fig. 6 The experimental UV spectrum at 25 °C of a 1,2-dichloroethane solution of $(EtNH)_2$dtlI (bottom) and that calculated for $(EtNH)_2$dtlI$_3$ (top)

similar thiuret compounds,[27] with the participation of the nonbonded p electrons of the sulphur atoms in the conjugated ring system. As far as the equilibrium of eqn. (5) is concerned, experimental difficulties, due to the instability of 1,2-DCE solutions of HI, prevented us from carrying out reliable measurements with which to study this equilibrium independently.

Kinetic Measurements.—The experimental conditions for the kinetic measurements, and the best-fit parameters obtained under a few different assumptions, are given in Table 4. The total explored $(EtNH)_2$dtm and I_2 concentration ranges were, respectively, (7.6×10^{-5})–(1.26×10^{-3}) mol dm^{-3}, and (1.25×10^{-5})–(6×10^{-3}) mol dm^{-3}, and the $(EtNH)_2$dtm to I_2 ratio varied from 79–1.2×10^{-2}. Independently measured values were used for many of the 14 parameters involved. In addition to the initial concentrations of the reactants, this was also the case for the molar extinction coefficients of all species involved (see Experimental section). Since it was impossible to measure directly the molar absorptivity of the HI_3 species, an identical value as for $(EtNH)_2$dtlI$_3$ was used. The formation constants for $(EtNH)_2$dtm·I_2, $K_1 = 2.3 \times 10^3$ dm^3 mol^{-1}, and for $(EtNH)_2$dtlI$_3$, $K_2 = 6.2 \times 10^5$ dm^3 mol^{-1}, were also fixed.

In a first stage, k_2 was maintained at zero and k_1 and K_3 were treated as fitting parameters. Values ranging from 0.79–0.96 s^{-1} for k_1 and from 8.14–9.42 × 10^6 dm^3 mol^{-1} for K_3 were thus calculated in runs 1*a*, 5*a*, 7*a* and 9*a*, for which closely fitting coincident calculated and experimental absorbance *vs.* time curves were obtained, with low s_0 values (see Experimental section). However, this simple kinetic scheme did not fit kinetic runs in which $[I_2]$ was in large excess with respect to $[(EtNH)_2$dtm], as shown by the completely different values obtained for k_1 in runs 18*a*, 19*a* and 20*b*. It must be stressed that in runs 13–20 K_3 was kept fixed to the average 8.93 × 10^6 dm^3 mol^{-1} value calculated for runs 1–12. All attempts to treat K_3 as a fitting parameter were in fact unsuccessful for runs carried out in the presence of a large I_2 excess, due to the complete complexation of $(EtNH)_2$dtlI and HI to the corresponding triiodides.

In order to explain fully the kinetics observed when $[I_2]$ exceeded $[(EtNH)_2$dtm], an additional second-order reaction,

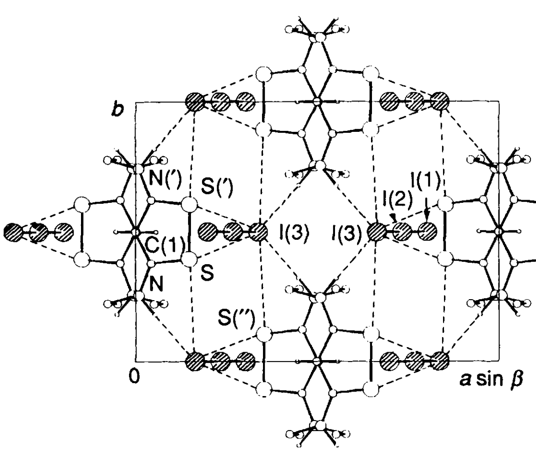


Fig. 7 Projection of the structure of $(EtNH)_2dtlI_3$ along [001]

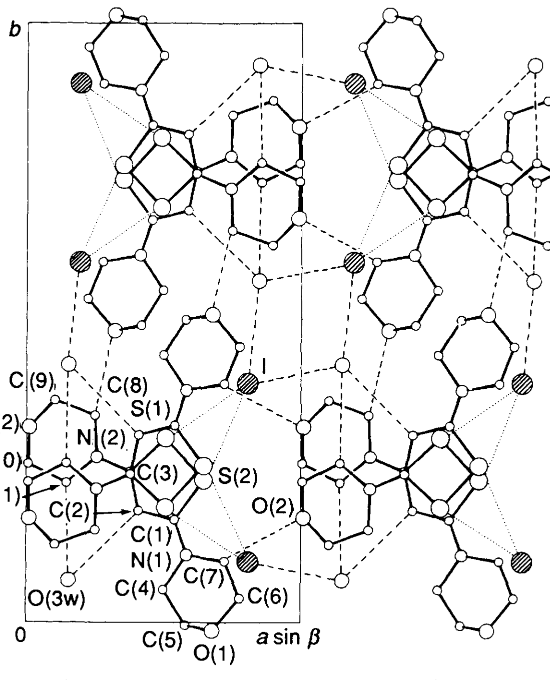


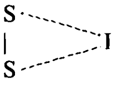
Fig. 8 Projection of the structure of $mo_2dtlI{\cdot}H_2O$ along [001]

first-order in both $[(EtNH)_2dtm{\cdot}I_2]$ and in free $[I_2]$ [eqn. (3)] was taken into account. Whereas this second-order reaction alone was unable to fit the kinetic data, as shown by the completely inconsistent k_2 values found in runs 4*a*, 17*a* and 20*a*, satisfactorily constant and consistently well-defined fittings were obtained for the full range of initial I_2 and $(EtNH)_2dtm$ concentrations when both the first- and the second-order kinetic paths were taken into account at once. Attempts at varying K_3, k_1 and k_2, or even k_1 and k_2 simultaneously, led to divergence of the fitting procedure. Reasonably constant values of K_3 and k_1 were obtained in runs 1–12, with a correlation coefficient never exceeding an acceptably low $r = 0.90$ value. Both these parameters were scarcely affected by putting $k_2 = 0$ or $k_2 = 2.0 \times 10^3$ dm^3 mol^{-1} s^{-1} (compare runs 1*b* to 1*a*, 5*b* to 5*a*, 7*b* to 7*a*, and 9*b* to 9*a*). This result can be attributed to the negligible importance of the second-order path when the free $[I_2]$ is much lower than that of $[(EtNH)_2dtm{\cdot}I_2]$. In fact, taking into account the reagents and the $[(EtNH)_2dtm{\cdot}I_2]$ equilibrium concentrations, the ratios of the initial rates for the first- (v_1) and second-order process (v_2) can be easily evaluated to range between 80 (run 1) and 7 (run 12). The second-order kinetic process appears instead to be important in runs 13–20, where the v_2 to v_1 ratio varied from 1 (run 13) to 3 (run 30*b*).

Reasonably constant k_2 values, ranging from 1.6×10^3 to 2.5×10^3 dm^3 mol^{-1} s^{-1}, were computed in runs 13–16, 17*b*, 18*b*, 19*b* and 20*c*, keeping K_3 and k_1 constant at the average values obtained from runs 1–12: $K_3 = 8.9(5) \times 10^6$ dm^3 mol^{-1} and $k_1 = 0.84(7)$ s^{-1}. The $k_2 = 2.0(3) \times 10^3$ dm^3 mol^{-1} s^{-1} average value calculated from these runs was in turn used as fixed parameter in runs 1–12 to recalculate final values for K_3 and k_1. Table 4 shows that such values were not affected significantly by this correction. A good agreement between the experimental and calculated absorbance *vs.* time curves was always found, as shown by s_o values ranging from 0.004–0.008 in runs 1–12 (except 4*a*), and from 0.012–0.020 absorbance units in runs 13 to 16, 17*b*, 18*b*, 19*b* and 20*c*. The latter runs involved in fact much larger absorbances (see Fig. 3), so that the relative error was almost constant.

In conclusion, both kinetic paths corresponding to eqns. (2) and (3) of Scheme 1 were found to be essential in order to fit the whole set of runs of Table 4, the first-order process being defined from kinetic data of reactions carried out with a $(EtNH)_2dtm$ excess, the second-order process increasing its importance with an increase in the free I_2 concentration.

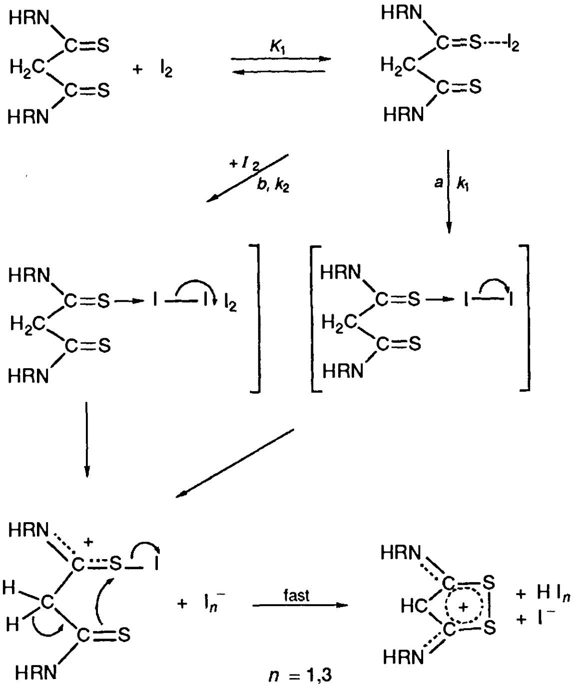
Description of Solid State Structures.—The structure of the salt $(EtNH)_2dtlI_3$ (Fig. 7) consists of chains running parallel to [010], in which the 3,5-bis(ethylamino)-1,2-dithiolylium cation and I_3^- anion are connected by two strong interactions of the terminal I(3) iodide atom of the unsymmetrical I_3^- ($I_2 \cdots I^-$) anion with both the sulphur atoms of the disulphide group in a triangular arrangement [I(3) ··· S = 3.634(3) Å, S ··· I(3) ··· S



= 33.0(1)°]. The other interactions in the chain involve the above cited I(3) through two hydrogen-bonds with the adjacent N atoms [I(3) ··· N('') = 3.595(8), I(3) ··· H(2'') = 2.58(11) Å, I(3) ··· H(2)-N = 176(8)° where (''): 1/2 − *x*, 1/2 − *y*, −*z*] and two weak contacts with two neighbouring sulphur atoms in an almost linear ··· I(3) ··· S–S ··· I(3) ··· S–S ··· I(3) ··· arrangement [I(3) ··· S('') = 3.864(4) Å, S–S ··· I(3) = 174.1(1)°, S ··· I(3) ··· S = 168.1(1)°]. The chains are held together by van der Waals contacts. Similar linear and triangular arrangements with distances S ··· X (X = Cl, Br, I, N) shorter than the corresponding van der Waals contacts are common enough and they were observed, for example, in 3,5-diamino-1,2-dithiolium iodide[28] and in the salts 4-phenyl-1,2-dithiolylium iodide,[29] chloride monohydrate,[30] bromide[31] and thiocyanate.[32] In the salt $mo_2dtlI{\cdot}H_2O$ (Fig. 8), layers lying approximately parallel to (201) are determined by contacts involving: (*a*) the anion and the cation through a triangular contact of the first with both the sulphur atoms of the disulphide group [I ··· S(1) = 3.571(3), I ··· S(2) = 3.641(2) Å; S(1) ··· I ··· S(2) = 32.8(1)°]; (*b*) the anion and the solvent molecule [I ··· O(3w)(1 − *x*, 1/2 + *y*, 1/2 − *z*) = 3.53(1), I ··· O(3w) (1 + *x*, 1/2 − *y*, 1/2 + *z*) = 3.71(1) Å; I ··· O(3w) ··· I = 109.9(3)°, O(3w) ··· I ··· O(3w) = 70.1(3)°]; (*c*) the cations related by symmetry operations through hydrogen bonds [C(7) ··· O(2) (1 + *x*, 1/2 − *y*, 1/2 + *z*) = 3.07(2), H(9) ··· O(2) = 2.26 Å; C(7)–H(9) ··· O(2) = 132°; C(8) ··· O(1) (1 − *x*, 1/2 + *y*, 1/2 − *z*) = 3.11(2), H(11) ··· O(1) = 2.27 Å; C(8)–H(11) ··· O(1) = 134°]; (*d*) the cation and the water molecule through weak interactions [C(2) ··· O(3w) = 3.41(2), H(1) ··· O(3w) = 2.40 Å; C(2)–H(1) ··· O(3w) = 170°; C(11) ··· O(3w) = 3.36(2), H(16) ··· O(3w) = 2.40 Å; C(11)–H(16) ··· O(3w) = 147°]. The dimensions in the cation of $(EtNH)_2dtlI_3$ (Fig. 1) are similar to those observed in the cation of the corresponding hexachlorostannate salt,[33] the only differences being the presence in $(EtNH)_2dtlI_3$ of a crystallographic mirror plane which passes through the C(2) atom and the midpoint of the S–S bond and of linear but very weak contacts ··· I(3) ··· S–S ··· I(3) ···. In the cation of $mo_2dtlI{\cdot}H_2O$ (Fig. 2) a pseudo-two-fold axis passes through the C(2) atom and the midpoint of the S–S bond. In both compounds $(EtNH)_2dtlI_3$ and $mo_2dtlI{\cdot}H_2O$ the five-membered ring is planar; in $(EtNH)_2dtlI_3$ the ethyl groups result roughly perpendicular to the ring [C(1)–N–C(3)–C(4) = −81(1)°], while in $mo_2dtlI{\cdot}H_2O$ the morpholinic rings, which show the usual distorted chair conformation, lie parallel to the above cited plane [S(2)–C(1)–N(1)–C(4) = 174.5(9)°, S(1)–C(3)–N(2)–C(11) = 176.3(8)°].

Discussion

On the basis of the results obtained we propose the reaction mechanism reported in Scheme 2.



Scheme 2

The first step is the formation of a 1 : 1 complex of the CT type between I_2 and $(EtNH)_2dtm$. This is not surprising, as CT complexes between halogens and thiones have been known for a long time.[34] They have also been invoked, and in some instances identified, as key intermediates in many redox reactions.[35] This CT complex undergoes transformation through electron donation from a sulphur atom to iodine with heterolytic fission of the I–I bond in the rate-determining step. This unimolecular process (*a*) accounts for the first-order kinetic term. The second-order term can be ascribed to the intervention of a free I_2 molecule assisting the I–I bond breaking in the CT complex, producing a more stable delocalized triiodine ion (*b*). The involvement of such a second-order term is not surprising. Similar kinetic behaviour has been demonstrated in the electrophilic bromination of alkenes in solvents of moderate polarity such as 1,2-dichloroethane, where the ionization of alkene–Br_2 CT complexes to bromonium ions is assisted by a second Br_2 molecule to give Br_3^- as the counter-anion.[21] A fast cyclization with expulsion of an acidic proton and an iodide anion to give the dithiolylium salt completes the reaction. A similar reaction mechanism involving initial 1:1 adduct formation between reagents, followed by a subsequent chelotropic rearrangement, has been invoked to explain the formation of the 3,5-bis(ethylamino)-1,2-dithiolylium cation when reacting $(EtNH)_2dtm$ with $SnCl_4$.[34] No kinetic or equilibrium studies are available on this reaction, but it seems that our results give support to the mechanism invoked.

The further associative equilibria of I_2 with 3,5-bis(ethylamino)-1,2-dithiolylium iodide (K_2) and with HI (K_3) are not drawn in Scheme 2 for brevity. The constant K_2 is lower than K_3 and both are lower than the value ($K = 10^{7.7}$ dm^3 mol^{-1}) reported for the $I^- + I_2 \rightleftharpoons I_3^-$ equilibrium in propylene carbonate.[36] However, this equilibrium constant shows marked differences depending on the solvent (in aqueous solution at 25 °C a value of 721 dm^3 mol^{-1} was found)[37] and on the counterion.[38] A further contribution for the different values obtained for K_2 and K_3 could arise if in 1,2-dichloroethane dithiolylium salts were present as ion pairs holding a triangular arrangement where the anion forms close contacts with both sulphur atoms of the dithiolylium cation, as found in the solid state. In this case the I^- anion of $(EtNH)_2dtlI$ would be more stabilized and therefore less available to interact with I_2.

The crystallographic studies of 1,2-dithiolylium halides, where the five-membered rings possessing a sextet of π-electrons are pseudo-aromatic, have allowed a detailed discussion of the relationships between the sulphur–sulphur bond and the S–S–C–X (X = C or N) torsion angles, bond order, type and position of the substituents. So it was observed that when the 1,2-dithiolylium cations are 3,5-unsubstituted[30] or 3,5-substituted with phenyl, 2-thienyl[39] or methylthio groups,[40] the conjugation is pronounced, extending over the sulphur–sulphur bond (in the range 2.00–2.03 Å), while the introduction of amino-substituents at the 3- and 5-positions leads to additional resonance forms and consequently to a shift of the conjugation from the S–S to the C–N bond. The results of the structural investigation of $(EtNH)_2dtlI_3$ and $mo_2dtlI{\cdot}H_2O$, which are *N,N′*-disubstituted and *N,N,N′N′*-tetrasubstituted derived 1,2-dithiolylium salts, respectively, confirm the influence of the amino-substituents on the conjugation; in addition, they indicate clearly that the weak linear halogen–sulphur contacts are very important for $(EtNH)_2dtlI_3$ in promoting a small but significant lengthening of the sulphur–sulphur bond [2.063(4) Å]. In $(EtNH)_2dtlI_3$ the I_3^- anion, which is of the type I–I ··· I^- [I(1)–I(2) = 2.741(2) Å, I(2)–I(3) = 3.141(2) Å] and nearly linear [I(1)–I(2)–I(3) = 177.4(1)°] lies on the crystallographic mirror-plane which passes through the cation. The iodine atom involved in contacts with the cation lies 0.510(2) and 0.011(1) Å from the plane of the 1,2-dithiolylium ring in $(EtNH)_2dtlI_3$ and $mo_2dtlI{\cdot}H_2O$, respectively.

Acknowledgements

This work was financed by grants from the Consiglio Nazionale delle Ricerche, from the Ministero della Pubblica Istruzione 40% and from the Regione Autonoma della Sardegna. The authors thank Dr. D. Atzei for experimental assistance.

References

1 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, 1987, ch. 2.
2 C. Raby, J. Claude, C. Moesch and J. C. R. Buxeraud, *Acad. Sci. Ser. C*, 1979, **288**, 319.
3 F. Bigoli, M. A. Pellinghelli, G. Crisponi, P. Deplano and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 1985, 1349.
4 D. Atzei, P. Deplano, E. F. Trogu, F. Bigoli, M. A. Pellinghelli and A. Vacca, *Can. J. Chem.*, 1988, **66**, 1483.
5 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem.*, 1989, **67**, 1416.
6 G. Crisponi, P. Deplano, V. Nurchi and E. F. Trogu, *Polyhedron*, 1984, **3**, 1241.
7 G. Crisponi, P. Deplano and E. F. Trogu, *Inorg. Chim. Acta*, 1984, **75**, 135.

8 G. Crisponi, P. Deplano and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 1986, 365.

9 F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 1987, 2407.

10 T. N. Lockyer and R. L. Martin, *Progress in Inorganic Chemistry*, ed. S. J. Lippard, vol. 27, p. 223, New York, 1980 and references therein.

11 E. Compaigne and R. D. Hamilton, *Q. Rep. Sulphur Chem.*, 1970, **5**, 275.

12 L. Menabue and G. C. Pellacani, *J. Chem. Soc., Dalton Trans.*, 1976, 455.

13 J. P. Guemas and H. Quinian, *Bull. Soc. Chim. Fr.*, 1973, 592.

14 S. Scheibye, B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 229.

15 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham., 1974, vol. IV, 99, 149.

16 G. Sheldrick, SHELX 76, A Program for Crystal Structure Determination, University of Cambridge, 1976.

17 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.

18 W. D. S. Motherwell, PLUTO, University of Cambridge, 1976.

19 C. K. Johnson, ORTEP, Report ORNL-3794, revised, Oak Ridge National Laboratory, Tennessee, 1965.

20 G. Bellucci, G. Berti, R. Bianchini, G. Ingrosso and R. Ambrosetti, *J. Am. Chem. Soc.*, 1980, **102**, 7480.

21 G. Bellucci, R. Bianchini and R. Ambrosetti, *J. Am. Chem. Soc.*, 1985, **107**, 2464.

22 W. C. Hamilton, *Statistics in Physical Science*, Ronald Press, New York, 1965.

23 Y. Bard, *Nonlinear Parameter Estimates*, Academic Press, New York, 1974.

24 W. E. Wentworth, *J. Chem. Educ.*, 1965, **42**, 96.

25 G. Bellucci, R. Bianchini, C. Chiappe, F. Marioni, R. Ambrosetti, R. S. Brown and H. Slebocka-Tilk, *J. Am. Chem. Soc.*, 1989, **111**, 2640.

26 R. Ambrosetti, G. Bellucci and R. Bianchini, *J. Phys. Chem.*, 1986, **90**, 6261.

27 R. T. Bailey, *J. Chem. Soc. A*, 1970, 1386.

28 A. Hordvik, *Acta Chem. Scand.*, 1965, **19**, 1039.

29 A. Hordvik and E. Sletten, *Acta Chem. Scand.*, 1966, **20**, 1874.

30 F. Grundtvig and A. Hordvik, *Acta Chem. Scand.*, 1971, **25**, 1567.

31 A. Hordvik and R. M. Baxter, *Acta Chem. Scand.*, 1969, **23**, 1082.

32 A. Hordvik and H. M. Kjoge, *Acta Chem. Scand.*, 1969, **23**, 1367.

33 M. G. B. Drew, J. M. Kisenyi and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1727.

34 F. A. Herbstein and W. Schwotzer, *J. Am. Chem. Soc.*, 1984, **106**, 2367.

35 E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev.*, 1978, **27**, 59.

36 C. A. Kovel and S. M. Drew, *Inorg. Chem.*, 1988, **27**, 4323.

37 R. W. Ramette and R. W. Sandford, *J. Am. Chem. Soc.*, 1965, **87**, 500.

38 R. T. Mahdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.*, 1983, 1071.

39 A. Hordvik, K. Jynge and I. Pedersen, *Acta Chem. Scand.*, 1981, **35**, 607.

40 G. Kiel, U. Reuter and G. Gattow, *Chem. Ber.*, 1974, **107**, 2569.

Paper 0/03476B
Received 31*st July* 1990
Accepted 3*rd October* 1990