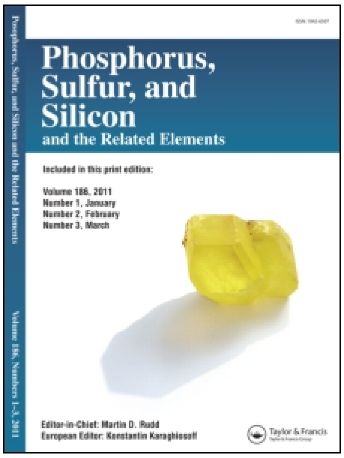

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SPECTROPHOTOMETRIC STUDY, CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:1 COMPLEX BETWEEN 1,3-DITHIOLANE-2-THIONE AND DIIODINE

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SPECTROPHOTOMETRIC STUDY, CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:1 COMPLEX BETWEEN 1,3-DITHIOLANE-2-THIONE AND DIIODINE

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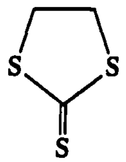
The reaction of 1,3-dithiolane-2-thione (dtt) with diiodine has been investigated by spectrophotometric methods in $CHCl_3$. The formation of a 1:1 charge-transfer complex between the reagents has been observed. The use of a general computer program has allowed to refine the formation constants and the extinction coefficients simultaneously in the whole 260–550 nm explored range. While the formation constant is rather lower ($K_{20^\circ} = 45 \pm 1$ mol^{-1} dm^3), the $-\Delta Ho$ is comparable with those generally found in other moderately strong thione-donors. An X-ray crystal structure analysis of the title compound has shown that the crystals are triclinic, space group $P\bar{1}$, with $a = 7.675(6)$, $b = 9.955(7)$, $c = 6.161(6)$ Å, $\alpha = 90.08(2)$, $\beta = 104.23(2)$, $\gamma = 95.18(2)^\circ$ and $Z = 2$. The molecular structure shows that the sulfur-thioamide atom of the ligand acts as the donor with respect to the diiodine molecule, and the S—I—I linkage is nearly linear [176.5(1)°]. The I—I bond length is 2.823(2) Å. The only significant changes in the bond lengths and angles of the ligand with the coordination are the distance of the neighboring C—C [1.44(2) Å], shorter than in the free ligand [1.493(4) Å] and consequently the S—C—C—S torsion angle [−14(2)°, −43.8(3)° in the free ligand].

Key words: Charge-transfer; diiodine; formation constants; X-ray; cyclic-thioketones.

INTRODUCTION

We are extensively investigating the donor properties of different molecules containing thiocarbonyl sulfur towards I_2. The formation of charge-transfer (c.t.) complexes between the reagents is generally observed. These c.t. complexes may be inert compounds[1,3] or intermediates in redox reactions where in many cases, the oxidation of the donor leads to interesting sulfur containing products and the reduction of the I_2 leads to a variety of polyiodides.[4,5] Solution studies give informations about the reaction mechanism, while solid-state spectroscopic studies supported by structural results, in addition to their intrinsic importance, give valuable informations about the amount of the charge-transfer from the donor to the acceptor, and about the sulfur-sulfur, sulfur-iodine, iodine-iodine, etc. interactions which are of current interest in the study of sulfur donors-iodine acceptor systems in organic charge-transfer metals.[6]

In this paper we report a study regarding the donor 1,3-dithiolane-2-thione (dtt), shown below:



RESULTS AND DISCUSSION

Solution Studies

Examples of spectrophotometric measurements obtained at 10°C in $CHCl_3$ using constant I_2 and increasing dtt concentration, and on the other hand using constant dtt and increasing I_2 concentration are reported in Figure 1 and Figure 2, respectively.

The u.v.-visible spectrum of these solutions is modified with respect to the addition spectrum of the pure reagents, however the features of the new produced species (c.t. band, etc.) are not immediately evident. By using the computer program "SUPERQUAD" previously described,[7] the extinction coefficients and the

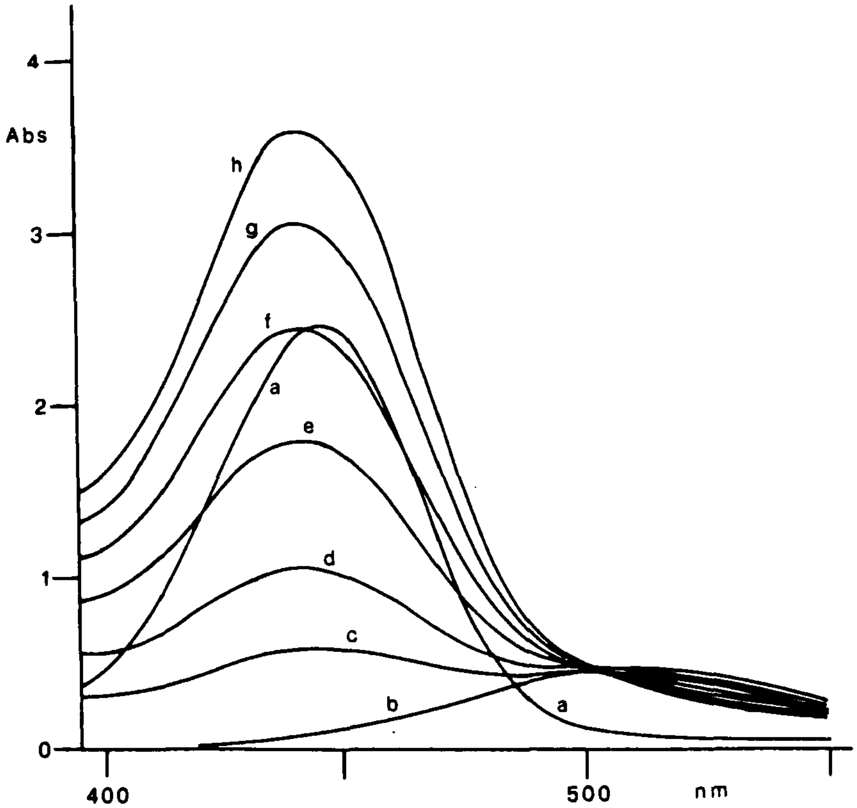


FIGURE 1 Visible spectra at 283 K in 1 cm cell of $CHCl_3$ solutions containing constant amounts of I_2 (5.0×10^{-4} mol dm^{-3}) and variable dtt concentrations in the ratios: b) 1:0; c) 1:5; d) 1:10; e) 1:20; f) 1:30; g) 1:40; h) 1:50. The spectrum of the ligand (2.5×10^{-2} mol dm^{-3}) is reported for comparison in plot a).

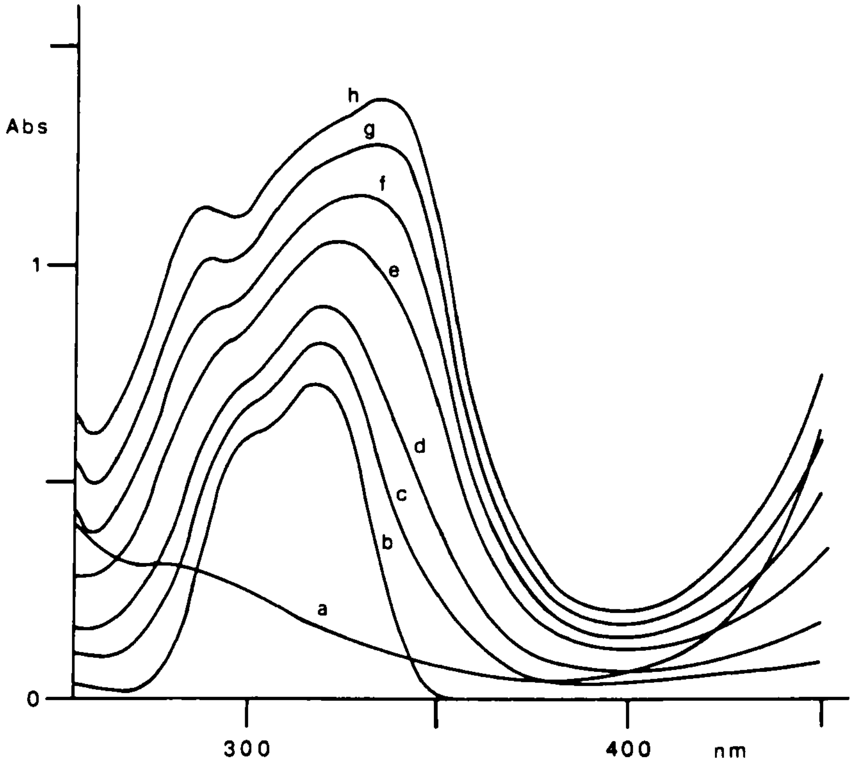


FIGURE 2 U.v.-visible spectra at 283 K in 0.1 cm cell of $CHCl_3$ solutions containing costant amounts of dtt (5.0×10^{-4} mol dm^{-3}) and variable I_2 concentrations in the ratios: b) 1:0; c) 1:5; d) 1:10; e) 1:20; f) 1:30; g) 1:40; h) 1:50. The spectrum of diiodine (2.5×10^{-2} mol dm^{-2}) is reported for comparison in plot a).

formation constants have been calculated simultaneously at different temperatures in the whole explored wavelength range. In every determination 200 absorbances, taken at 30 different wavelengths, have been used. Experimental measurements are interpreted quite satisfactorily by assuming that the reagents are in equilibrium with a 1 : 1 complex. In Figure 3, the calculated spectrum of this complex is reported. The features of the spectrum: a new intense band at 340 nm (c.t. band), blue shifting of the ligand and diiodine bands at 280 and 430 nm respectively, show that the complex is of a charge-transfer type.[8]

In Table I logK and the values of enthalpy and entropy changes (obtained by interpolation of the plot logK versus $1/T$, correlation coefficient greater than 0.99) are reported.

While the formation constant is rather low, the enthalpy change is comparable with those generally found in thione-donors, and it shows, in accordance with the blue-shifting of the diiodine band, that the interaction of dtt with I_2 is moderately strong.

A previous study on this equilibrium in cyclohexane, has been reported a long time ago.[9] The authors calculated at 460 nm a formation constant which is in accordance with the value reported by us in $CHCl_3$. However, they were not able to recognize the features of the c.t.-complex, and indeed they wrongly concluded

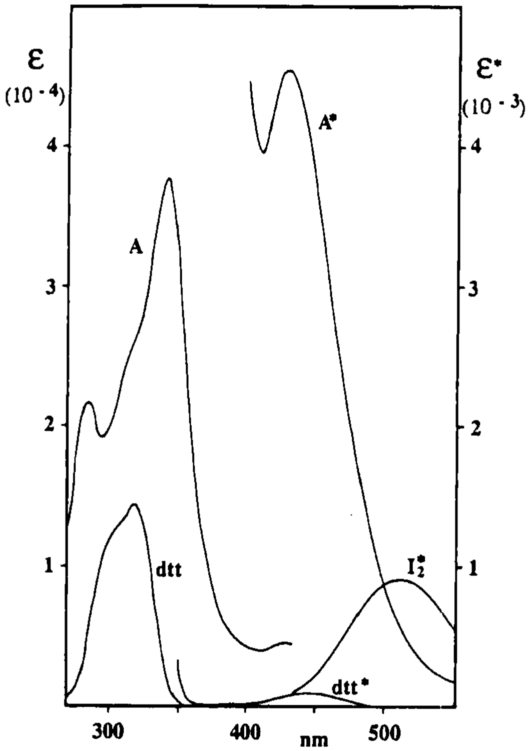


FIGURE 3 Calculated u.v.-visible spectra of the 1:1 complex (A) between dtt and I_2 at 283 K in $CHCl_3$ solutions. The spectra of the free reagents are reported for comparison.

TABLE I

Logarithms of the equilibrium constants (standard deviations in parentheses), enthalpy and entropy changes for the formation of 1:1 complex between I_2 and dtt in $CHCl_3$ solutions

T °C	log K
30	1.48(2)
25	1.56(1)
20	1.65(1)
15	1.73(1)
10	1.81(1)

ΔH_o = -6.8(4) Kcal mol^{-1} ; ΔS_o = -16(1) cal K^{-1} mol^{-1}

about the blue-shifting of the diiodine band and consequently about the interaction strength of dtt with I_2.

According to Literature[10] i.r. spectroscopic results (see Experimental) reflect the lowering of the C═S bond order, as a consequence of the coordination with I_2, since the absorption at 1065 cm^{-1} attributed to the C═S stretching is shifted to 1037 cm^{-1} in the complex. X-ray structural results (see below) confirm that the sulfur-thioamide atom is the donor towards I_2, however no appreciable change in the C═S bond length is observed as a consequence of the coordination. We conclude that the band at 1065 cm^{-1}, which exhibits a ≈30 cm^{-1} shift to lower wave-

TABLE II

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	X/a	Y/b	Z/c		X/a	Y/b	Z/c
I(1)	2093(1)	2769(1)	1167(1)	S(3)	3036(6)	-576(3)	1030(6)
I(2)	2143(1)	4501(1)	-2446(1)	C(1)	2513(16)	-410(12)	3539(18)
S(1)	1908(5)	992(3)	4459(6)	C(2)	3129(24)	-2989(15)	3133(26)
S(2)	2566(7)	-1842(4)	5048(6)	C(3)	3612(27)	-2272(14)	1300(26)

TABLE III

Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

I(1)-I(2)	2.823(2)	I(2)-I(1)-S(1)	176.5(1)
I(1)-S(1)	2.715(4)	I(1)-S(1)-C(1)	103.7(4)
S(1)-C(1)	1.65(1)	S(1)-C(1)-S(2)	121.0(7)
S(2)-C(1)	1.70(1)	S(1)-C(1)-S(3)	124.2(7)
S(3)-C(1)	1.70(1)	S(2)-C(1)-S(3)	114.8(7)
S(2)-C(2)	1.79(2)	C(1)-S(2)-C(2)	99.8(7)
S(3)-C(3)	1.78(2)	C(1)-S(3)-C(3)	97.9(7)
C(2)-C(3)	1.44(2)	S(2)-C(2)-C(3)	110.6(1.1)
		S(3)-C(3)-C(2)	115.3(1.2)

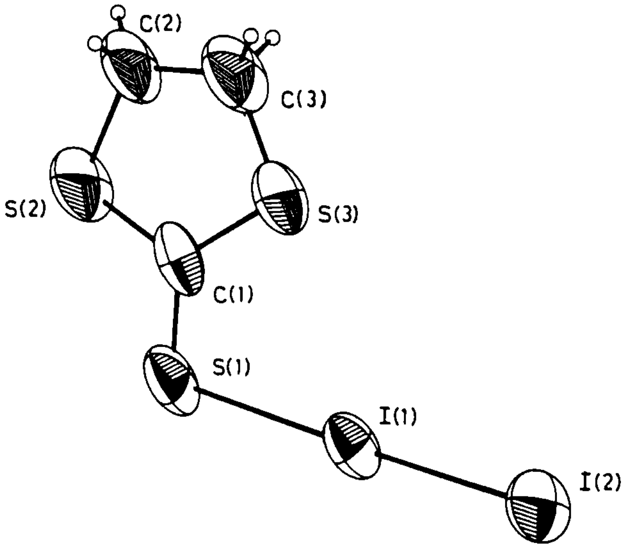


FIGURE 4 Perspective view of the molecule.

numbers should not be connected with the C=S stretching mode only, but also with other ring vibrations which undergo modification as a consequence of the coordination.

Structural Results

Fractional atomic coordinates are given in Table II, bond distances and angles are reported in Table III. The molecular structure of this neutral molecular compound

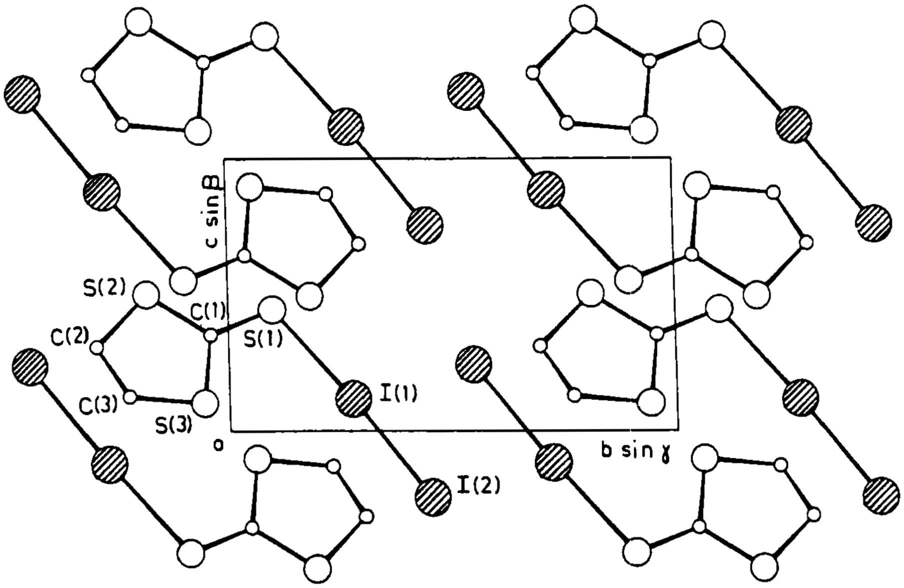


FIGURE 5 Projection of the structure along [100].

and the corresponding atom labelling scheme are shown in Figure 4. In the ligand moiety the values of the bond lengths and angles are similar to those observed in the free ligand[11] except the C(2)-C(3) distance [1.44(2) Å] which is shorter than in the free ligand [1.493(4) Å] and, as a consequence, the S(2)-C(2)-C(3)-S(3) torsion angle is smaller [−14(2) in the coordinated, −43.8(3)° in the free ligand]. The CS_3I moiety is planar [maximum deviation from the mean weighted plane −0.020(13) Å at C(1)]; the I(2) atom departs by 0.138(2) Å from this plane. The formation of the complex does not bring appreciable change in the exocyclic C(1)-S(1) bond length. The correlation between the S(1)-I(1) and I(1)-I(2) distances is observed as already reported in similar cases by us[2] and others.[12] The C(1)-S(1)-I(1) angle of 103.7(4)° lies in the 92–110° normal range and the S(1)-I(1)-I(2) linkage is nearly linear [176.5(1)°]. There are no intermolecular contacts less than the sums of the van der Waals radii. The projection of the crystal structure is given in Figure 5.

EXPERIMENTAL

Materials

Dtt was obtained from Aldrich and used after recrystallization from diethyl ether; bisublimed I_2 was Carlo Erba RPE; $CHCl_3$ was Carlo Erba RPE ACS grade and used after dehydration over molecular sieves 4 A. Well formed lustrous red-brown crystals of dtt·I_2 have been obtained on slow evaporation of an equimolecular mixture of the reagents in CH_2Cl_2/petroleum ether 40/60°.
Analytical results: Found: C 9.37 H 0.60 S 24.82
Calc. For $C_3H_4S_3I_2$: C 9.24 H 1.03 S 24.66

Spectroscopic measurements

I.r. spectra (cm^{-1}) were recorded on a Perkin Elmer mod. 983 Spectrophotometer as KBr pellets: 1410 m 1278 m 1248 m 1150 m 1037 vs 1018 s 945 br 910 sh 895 ms 828 m 663 m 512 m 450 m 380 ms 282 m 245 m.

The electronic spectra were measured at various temperatures (±0.1C) in the range 10–30°C in

TABLE IV

Experimental data for the crystallographic analyses

formula		$C_3H_4S_3I_2$
$\underline{M}$		390.054
crystal system		triclinic
space group		$P\bar{1}$
$\underline{a}$/Å		7.675(6)
$\underline{b}$/Å		9.955(7)
$\underline{c}$/Å		6.161(6)
α/deg		90.08(2)
β/deg		104.23(2)
γ/deg		95.18(2)
$\underline{V}$/Å^3		454.3(7)
$\underline{Z}$		2
Dc/Mg m^{-3}		2.85
$\underline{F}$(000)		352
temperature/K		295
crystal size/mm		0.65x0.23x0.19
diffractometer		Siemens AED
μ(Mo K_α)/cm^{-1}		74.31
scan type		θ/2θ
scan speed/deg min^{-1}		2.5–12
scan width/deg		1.10+0.346 tgθ
radiation		Nb-filtered MoKα ($\bar{\lambda}$ = 0.71073 Å)
θ-range		3–27
reflections for lattice parameters	number	30
	θ-range	10–18
std reflcn measured after every 50		-1 5 2
h range		-12 12
k range		-15 15
l range		0 10
no. of meas.refl.		1985
condition for obs.		$\underline{I}>2\sigma(\underline{I})$
no. reflections used in the refinement		1192
no.refined parameters		74
$\underline{R}^a$ ($\underline{R}w^a$)		0.0564 (0.0811)
k,g ($w = K/\left[\sigma^2(\underline{F}_o)+g\underline{F}^2_o\right]$)		0.1696 0.360200
min/max height in final Δ F(eA^{-3})		-2.06/1.70

(a) $\underline{R} = \sum\left|\Delta \underline{F}\right| / \left|\underline{F}_o\right|$; $\underline{R}w = \left[\sum \underline{w}(\Delta\underline{F})^2/\sum \underline{wF}_o^2\right]^{1/2}$

CHCl$_3$ solutions with a Varian model Cary 2300 Spectrophotometer, equipped with an automatic system of data acquisition (DS15). A set of solutions containing a constant diiodine concentration (5.0 × 10^{-4} mol dm^{-3}) and variable dtt concentrations, ranging from 2.5 × 10^{-3} to 2.5 × 10^{-2} mol dm^{-3}, was used and the spectra recorded between 400 and 550 nm using 1 cm silica cells (see Figure 1). Another set of solutions was prepared with a constant dtt concentration (5.0 × 10^{-4} mol dm^{-3}) and variable diiodine concentrations, ranging from 2.5×10^{-3} to 2.5×10^{-2} mol dm^{-3}, in 0.1 cm silica cells in the 260–450 nm range (see Figure 2).

Calculations

The experimental points used in the calculations have been taken from the recorded spectra at 10 nm intervals and the total number was 200 readings for each system at each temperature. A program derived from "SUPERQUAD" as previously described[3] has been used to refine simultaneously equilibrium constants and molar extinction coefficients from the spectrophotometric data.

Structure determination

A crystal of dimensions $0.65 \times 0.23 \times 0.19$ mm was used. Cell dimensions were determined by least-squares refinement using the setting angle of 30 reflections in the range $10 \leq \Theta \leq 18°$. Observations were collected at 22°C using a Siemens AED diffractometer with Nb-filtered Mo-Kα radiation in the $\Theta/2\Theta$ scan mode (with Θ in the 3–27° range) giving 1985 measurements of which 1192 having $I \geq 2\sigma(I)$ were considered observed and used in the analysis. The space group was $P\bar{1}$. Intensity data were corrected for the Lorentz-polarization factor, for absorption (maximum and minimum values 1.50867, 0.67520) and extinction (maximum and minimum values 1.06550, 0.94711) using the empirical method of Walker and Stuart.[13] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters for all the non-hydrogen atoms using the SHELX 76 program.[14] The coordinates of the hydrogen atoms placed at their geometrically calculated positions were not refined, but introduced in the final structure factor calculation with fixed isotropic thermal parameters ($U = 0.1275$ Å^2). Convergence was reached at $R = 0.0564$.

Crystal data. $C_3H_4S_3I_2$, $M = 390.054$. Triclinic, space group $P\bar{1}$, $a = 7.675(6)$, $b = 9.955(7)$, $c = 6.161(6)$ Å, $\alpha = 90.08(2)$, $\beta = 104.23(2)$, $\gamma = 95.18(2)°$. $V = 454.3(7)$ Å^3, $Z = 2$, μ[Mo-Kα] = 74.31 cm^{-1}, $F(000) = 352$, $\lambda = 0.71073$ Å. Experimental data for the crystallographic analysis are summarized in Table IV.

Note: The tables of experimental data for the crystallographic analysis, of coordinates for the hydrogen atoms, and anisotropic thermal parameters are deposited with the Cambridge Crystallographic Data Center (CCDC) U.K.

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