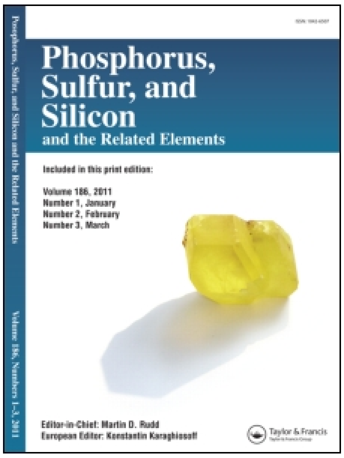

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A STUDY ON THE DONATING PROPERTIES OF 4,5,6,7-TETRATHIOCINO[1,2-b:3,4-b']- DIIMIDAZOLYL-1,3,8,10-TETRAPHENYL-2,9- DITHIONE(Ph_4todit) TOWARDS I_2. CRYSTAL AND MOLECULAR STRUCTURE OF Ph_4todit - $CHCl_3$

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A STUDY ON THE DONATING PROPERTIES OF 4,5,6,7-TETRATHIOCINO[1,2-b:3,4-b′]-DIIMIDAZOLYL-1,3,8,10-TETRAPHENYL-2,9-DITHIONE(Ph$_4$todit) TOWARDS I$_2$. CRYSTAL AND MOLECULAR STRUCTURE OF Ph$_4$todit · CHCl$_3$

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The X-ray structure of Ph$_4$todit · CHCl$_3$ (the title molecule) has shown that the crystals are monoclinic, space group $P2_1/n$, $a = 13.393(5)$, $b = 20.764(6)$, $c = 12.286(5)$ Å, $\beta = 97.88(2)°$, $V = 3384(2)$ Å^3, $Z = 4$. Solution and refinement of intensity data gave final residuals of R = 0.0551 and Rw = 0.0680, using 2958 observed reflections [$I \geq 2\sigma(I)$]. A comparison with the previously reported structural data of the corresponding tetraethyl substituted compound (Et$_4$todit) shows that the only significant differences are observed for the N—C—C—N torsion angle (63.5(7)°, −70(1)° in the Et derivative), and for the values of the torsion angles indicating the orientation of the substituents with respect to the imidazoline ring plane.

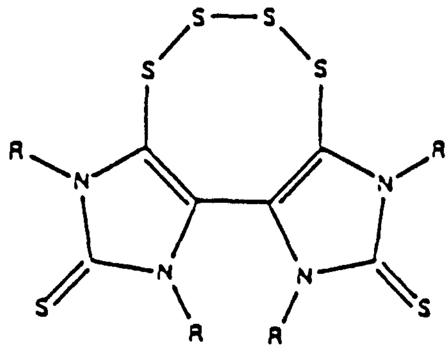
A spectrophotometric study on the reaction between diiodine and Ph$_4$todit in CHCl$_3$ has shown the formation of a 1:1 charge-transfer complex. A computer program has been used to refine the formation constant at six different temperatures and the extinction coefficients in the 260–520 nm range. The enthalpy of formation ($\Delta H° = -3.9(2)$ Kcal mol^{-1}) falls in usual thione-diiodine complexes range.

In the solid state a microcrystalline solid characterized as Ph$_4$todit · 2I$_2$ · 2CHCl$_3$ has been isolated. FT-Raman spectra on this solid compound show a very strong band attributed to ν(I—I) at 172 cm^{-1}. A comparison with the donor behaviour of Et$_4$todit shows that the very small differences detected by means of u.v. visible measurements, suggesting the sequence order Et$_4$todit > Ph$_4$todit, are supported by FT-Raman results, which indicate that the donation of Et$_4$todit produces a lengthening of the I—I distance (ν(I—I) at 147 cm^{-1}) larger than in Ph$_4$todit.

Key words: Charge-transfer; diiodine; formation constants; X-ray; imidazolyl-thiones.

INTRODUCTION

We have recently synthesized the new class of molecules 4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetrasubstituted-2,9-dithiones,[1] drawn below for reasons of clarity:



These molecules show interesting coordinative properties towards transition metals and diiodine.

A variety of metal-complexes where the ligand acts as a bidentate-bridging ligand has been isolated, and either linear[2,3] or not[4] polymers have been identified by means of X-ray diffraction studies.

Also the formation of charge-transfer (c.t.) complexes with diiodine has been observed. In the R = Et case, a 1:1 c.t. complex has been detected in $CHCl_3$ solutions, and a 1:2 (donor to acceptor) complex has been isolated in the solid state.[6]

It seemed interesting to us to investigate whether or not structural modifications are observed on varying the substituents, and possibly to correlate the coordinative properties with structural data.

In this paper we report an X-ray diffraction study on a crystal of Ph_4todit · $CHCl_3$, and a study on its coordinative properties towards I_2.

RESULTS AND DISCUSSION

Structure of Ph_4todit · $CHCl_3$

Fractional atomic coordinates are given in Table I, selected bond distances and angles are reported in Table II. The geometry of the organic molecule (Figure 1) agrees with that observed in the corresponding tetraethyl substituted molecule whether it is complexed[2-5] or not.[1] The only significant differences are observed for the N—C—C—N torsion angle and for the orientations of the substituents with respect to the imidazoline ring plane. In fact the torsion angle N—C—C—N determined by the substituents is in this case 63.5(7)°, while the corresponding values in the above cited compounds fall in the −70(1)°, 76(2)° range. Also the values of the torsion angles indicating the orientation of the phenyl groups with respect to the corresponding imidazoline ring plane are 56.5(8), −66.5(9), 55.3(9) and −79.4(8)°, while in Et_4todit case the corresponding values of the ethyl substituents, lying perpendicular and mutually opposite to the imidazoline ring plane, are in the 83(2)°, 92(2)° range. The analogies concern the chair conformation of the eight-membered ring, the presence of a pseudo two-fold axis, the rough planarity of the imidazoline rings, and the single-bond character for the distance (1.450(7)Å) between two sp^2-hybridized C(31), C(32) carbon atoms. The crystal structure (Figure

TABLE I

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

	X/a	*Y/b*	*Z/c*		*X/a*	*Y/b*	*Z/c*
S11	7319(1)	433(1)	1846(1)	C6C	5246(5)	−2281(3)	1891(5)
S21	4069(1)	290(1)	4108(1)	C1D	1423(4)	−1240(3)	1035(5)
S31	3060(1)	969(1)	3365(1)	C2D	1217(5)	−1375(3)	−59(6)
S12	2747(1)	−2498(1)	1826(1)	C3D	225(6)	−1346(4)	−565(6)
S22	2515(1)	96(1)	1174(1)	C4D	−522(6)	−1194(4)	19(8)
S32	1919(1)	448(1)	2528(1)	C5D	−311(6)	−1058(5)	1118(8)
N11	5648(3)	−320(2)	1858(4)	C6D	690(5)	−1092(4)	1656(6)
N21	5765(3)	465(2)	3056(4)	C	914(6)	1281(4)	5151(7)
N12	4012(3)	−1453(2)	2191(4)	Cl1	1532(2)	688(1)	6007(2)
N22	2467(3)	−1214(2)	1527(4)	Cl2	−55(2)	927(1)	4246(2)
C11	6249(4)	188(2)	2266(5)	Cl3	447(2)	1870(2)	5926(2)
C21	4852(4)	146(2)	3127(4)	H	1557(41)	1448(24)	4847(42)
C31	4786(4)	−341(2)	2375(4)	H2A	7333(45)	−1027(28)	1796(49)
C12	3082(4)	−1727(3)	1845(4)	H3A	7546(45)	−1838(29)	477(48)
C22	3006(4)	−635(3)	1668(5)	H4A	6348(45)	−1918(29)	−1125(51)
C32	3962(4)	−790(2)	2094(4)	H5A	4785(48)	−1380(32)	−1200(54)
C1A	5859(4)	−756(2)	1014(5)	H6A	4532(49)	−666(30)	51(52)
C2A	6750(4)	−1101(3)	1136(5)	H2B	5085(50)	1579(33)	3177(55)
C3A	6902(5)	−1543(3)	347(6)	H3B	5419(47)	2441(32)	4233(53)
C4A	6177(5)	−1651(3)	−547(6)	H4B	6809(46)	2322(31)	5664(54)
C5A	5296(5)	−1304(3)	−670(5)	H5B	7796(48)	1419(30)	5707(54)
C6A	5136(4)	−852(3)	119(5)	H6B	7304(53)	648(33)	4449(61)
C1B	6107(5)	1008(3)	3720(5)	H2C	5268(48)	−1363(32)	4038(55)
C2B	5554(6)	1569(3)	3645(6)	H3C	6688(48)	−1882(29)	4484(52)
C3B	5825(8)	2075(4)	4352(7)	H4C	7245(49)	−2602(30)	3465(51)
C4B	6657(9)	2021(5)	5109(8)	H5C	6358(45)	−2933(30)	1722(50)
C5B	7250(7)	1476(5)	5176(7)	H6C	4793(45)	−2401(29)	1116(54)
C6B	6959(6)	964(4)	4477(6)	H2D	1743(47)	−1509(29)	−589(52)
C1C	4914(4)	−1811(3)	2561(5)	H3D	92(46)	−1538(31)	−1327(54)
C2C	5468(5)	−1653(3)	3557(5)	H4D	−1317(51)	−1163(30)	−390(53)
C3C	6374(5)	−1965(4)	3865(6)	H5D	−771(49)	−925(30)	1605(52)
C4C	6709(6)	−2417(4)	3202(8)	H6D	871(46)	−999(29)	2453(55)
C5C	6152(5)	−2584(3)	2226(7)				

2) consists of a three dimensional network, where the most significant interactions are of type S $\cdots$ S[S(12) $\cdots$ S(31) (1/2 − x, y − 1/2, 1/2 − z) 3.360(3), S(21) $\cdots$ S(21) (1 − x, −y, 1 − z) 3.313(2) Å], S $\cdots$ C_{phenyl}[S(21) $\cdots$ C(6B) (1 − x, −y, 1 − z) 3.515(9)Å], and C_{phenyl} $\cdots$ C_{phenyl}[C(3B) $\cdots$ C(2C) (1 − x, −y, 1 − z) 3.404(12), C(4C) $\cdots$ C(2D) (1/2 + x, −y − 1/2, 1/2 + z) 3.417(12)Å].

Diiodine Complexes

The donor capability of the Ph_4todit molecule has been investigated in $CHCl_3$ solutions by means of uv-visible spectrophotometric measurements.

The addition of I_2 to Ph_4todit produces a drastic change in the uv-visible spectrum of the solution: a new strong band appears at 370 nm, the characteristic band of the I_2 is blue shifted and occurs as a shoulder on the low frequency side of the 370 nm band. These features show that the complex between the reagents is of the c.t. type.[6] The spectrophotometric measurements obtained in the 260–520 nm range, using constant Ph_4todit concentration (4.8 × 10^{-4} mol dm^{-3}) and increasing I_2

TABLE II

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

a) ligand molecule without phenyl groups:

S21—S31	2.076(2)	C11—N11—C31	109.7(4)
S31—S32	2.033(2)	C11—N11—C1A	125.7(5)
S22—S32	2.074(2)	C31—N11—C1A	124.6(4)
S11—C11	1.668(6)	C11—N21—C21	110.4(4)
S21—C21	1.729(6)	C11—N21—C1B	126.3(5)
S12—C12	1.662(7)	C21—N21—C1B	123.4(5)
S22—C22	1.731(6)	C12—N12—C32	110.6(4)
N11—C11	1.379(6)	C12—N12—C1C	124.5(5)
N11—C31	1.393(7)	C32—N12—C1C	124.8(4)
N11—C1A	1.434(7)	C12—N22—C22	110.6(4)
N21—C11	1.366(8)	C12—N22—C1D	126.8(5)
N21—C21	1.404(7)	C22—N22—C1D	122.4(5)
N21—C1B	1.430(8)	N21—C21—C31	106.5(5)
N12—C12	1.382(7)	N21—C21—S21	125.4(4)
N12—C32	1.383(6)	C31—C21—S21	127.7(4)
N12—C1C	1.438(7)	N11—C31—C21	107.8(5)
N22—C12	1.370(7)	N11—C31—C32	124.3(4)
N22—C22	1.401(7)	C21—C31—C32	127.9(5)
N22—C1D	1.446(7)	N12—C32—C31	126.4(4)
C21—C31	1.364(6)	N12—C32—C22	107.6(4)
C22—C32	1.354(7)	C31—C32—C22	126.0(5)
C31—C32	1.450(7)	N22—C22—C32	106.7(5)
S11—C11—N11	127.2(4)	N22—C22—S22	123.0(4)
S11—C11—N21	127.1(4)	C32—C22—S22	129.6(5)
S12—C12—N12	129.1(5)	C21—S21—S31	103.4(2)
S12—C12—N22	126.5(4)	S21—S31—S32	105.1(1)
N11—C11—N21	105.7(4)	S31—S32—S22	104.4(1)
N12—C12—N22	104.4(5)	S32—S22—C22	101.4(2)

b) phenyl groups	i = A j = 11	i = B j = 21	i = C j = 12	i = D j = 22
C1i—C2i	1.382(8)	1.377(9)	1.381(8)	1.364(9)
C1i—C6i	1.376(8)	1.373(10)	1.389(9)	1.359(10)
C2i—C3i	1.370(9)	1.380(11)	1.382(10)	1.389(10)
C3i—C4i	1.381(9)	1.355(14)	1.359(12)	1.346(12)
C4i—C5i	1.373(9)	1.379(15)	1.367(12)	1.370(14)
C5i—C6i	1.387(9)	1.389(12)	1.379(9)	1.413(10)
Nj—C1i—C2i	120.1(5)	120.1(6)	118.9(5)	118.2(5)
Nj—C1i—C6i	118.9(5)	120.4(6)	120.0(5)	119.2(6)
C2i—C1i—C6i	120.9(5)	119.4(6)	121.0(6)	122.4(6)
C1i—C2i—C3i	118.7(6)	120.6(7)	118.4(6)	119.0(7)
C2i—C3i—C4i	121.0(6)	119.3(8)	120.6(7)	120.5(8)
C3i—C4i—C5i	120.2(6)	121.5(9)	121.0(7)	120.4(8)
C4i—C5i—C6i	119.4(6)	118.8(9)	119.9(7)	120.3(8)
C5i—C6i—C1i	119.8(5)	120.3(8)	119.0(6)	117.5(7)

c) trichloromethane molecule:

C—Cl1	1.752(8)	Cl1—C—Cl2	109.5(5)	Cl1—C—H	96(3)
C—Cl2	1.751(8)	Cl1—C—Cl3	110.2(5)	Cl2—C—H	119(3)
C—Cl3	1.720(9)	Cl2—C—Cl3	110.9(5)	Cl3—C—H	110(3)
C—H	1.04(6)				

concentrations, showed two isosbestic points at 282 and 308 nm related to the equilibrium between the free- and the complexed-ligand, in the solutions where the I_2 absorbance is negligible (Figure 3). The symmetrical measurements using

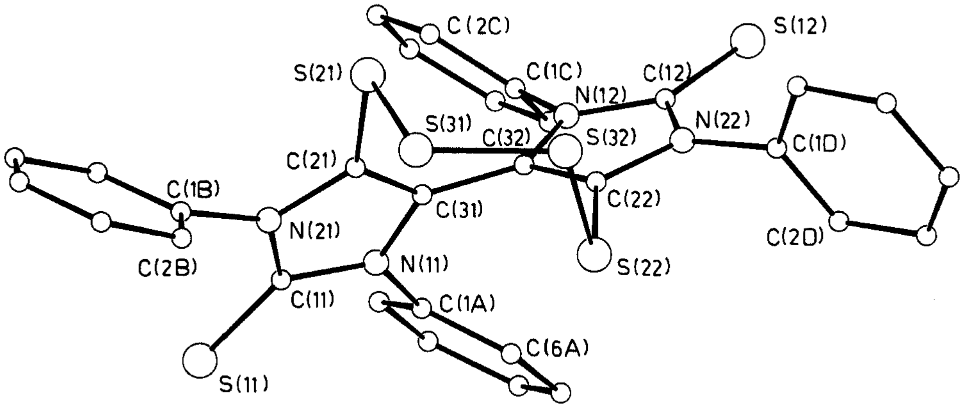


FIGURE 1 Perspective view of the molecule with non-hydrogen atoms numbering scheme.

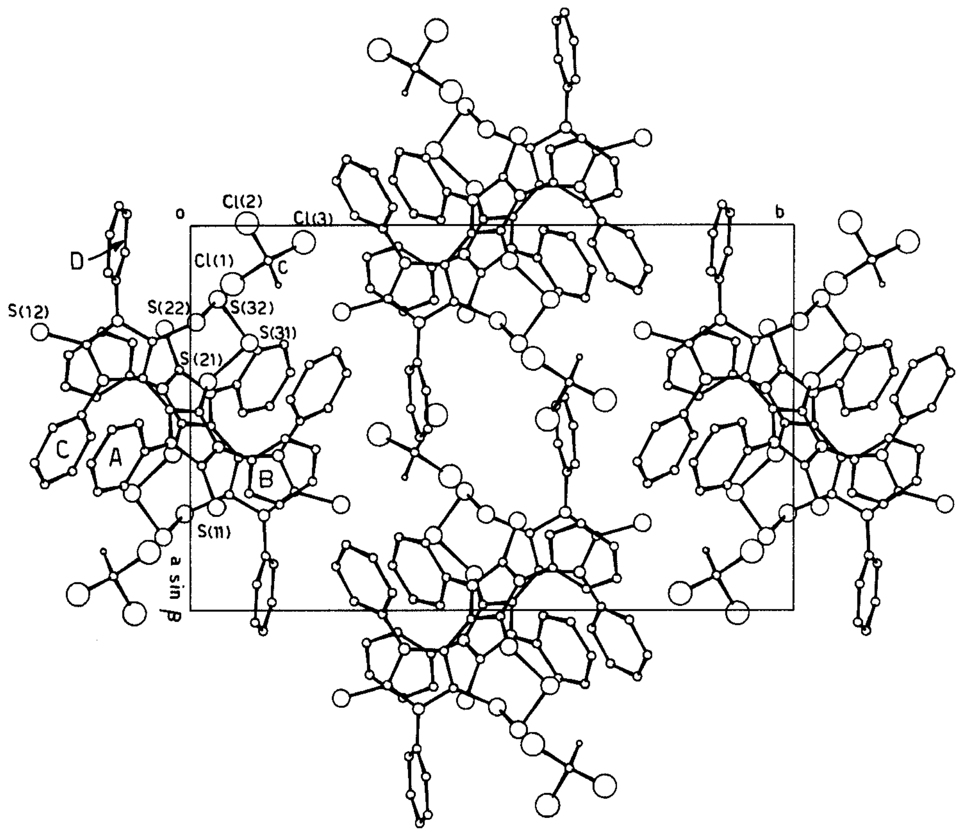


FIGURE 2 Projection of the structure viewed along c.

constant I_2 concentration (4.8×10^{-4} mol dm^{-3}) and increasing Ph_4todit concentrations in the 550–450 nm range, showed also the existence of an isosbestic point at 510 nm (Figure 4), however they were not used in the calculations since the

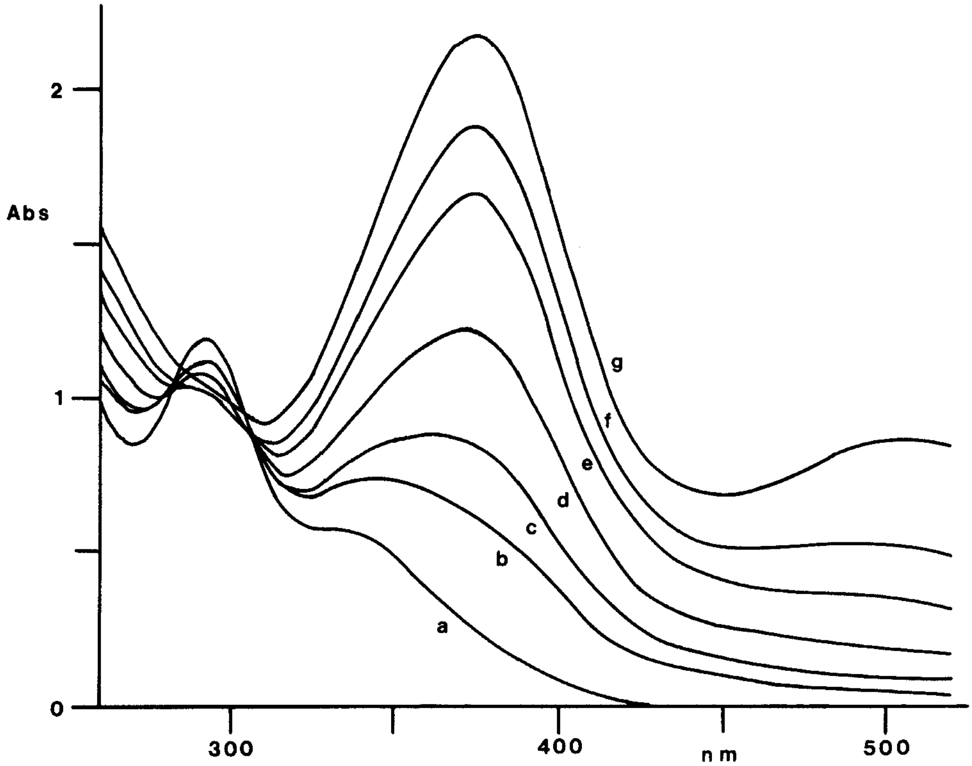


FIGURE 3 U.v.-visible spectra at 283 K in 0.1 cm cell of $CHCl_3$ solutions containing constant amounts of Ph_4todit (4.8×10^{-4}) and variable I_2 concentrations in the ratios: a = 1:0, b = 1:1, c = 1:2, d = 1:4, e = 1:8, f = 1:12, g = 1:20.

absorbance variations were much lower than in the former set, which therefore was judged more suitable for the calculations. The spectrophotometric data have been used to calculate simultaneously the extinction coefficients and the formation constants by means of a computer program "SUPERQUAD" previously described.[5] Experimental data are interpreted quite satisfactorily by assuming that the 1:1 species is the only complex present, as suggested by the existence of well defined isosbestic points. The refined molar extinction coefficients of the c.t. complex are plotted in Figure 5, and the obtained log K values are listed in Table III. The interpolation of the plot of log K versus 1/T (correlation coefficient greater than .99) allowed to obtain the enthalpy and the entropy changes (reported in Table III) for the 1:1 complex formation. No stoichiometries higher than 1:1 in $CHCl_3$ solutions are consistent with the measurements in the explored concentration range.

In the solid state a red-brown microcrystalline solid has been isolated on slow evaporation of $CHCl_3$ solution of the reagents. Analytical and spectroscopic results are in accordance with a Ph_4todit · $2I_2$ · $2CHCl_3$ formulation. Unfortunately no crystals suitable for X-ray diffraction studies could be obtained. However all the features of the complex and the analogies with the one of Et_4todit, show that, very likely, thione sulphur has the donor role in the molecule.

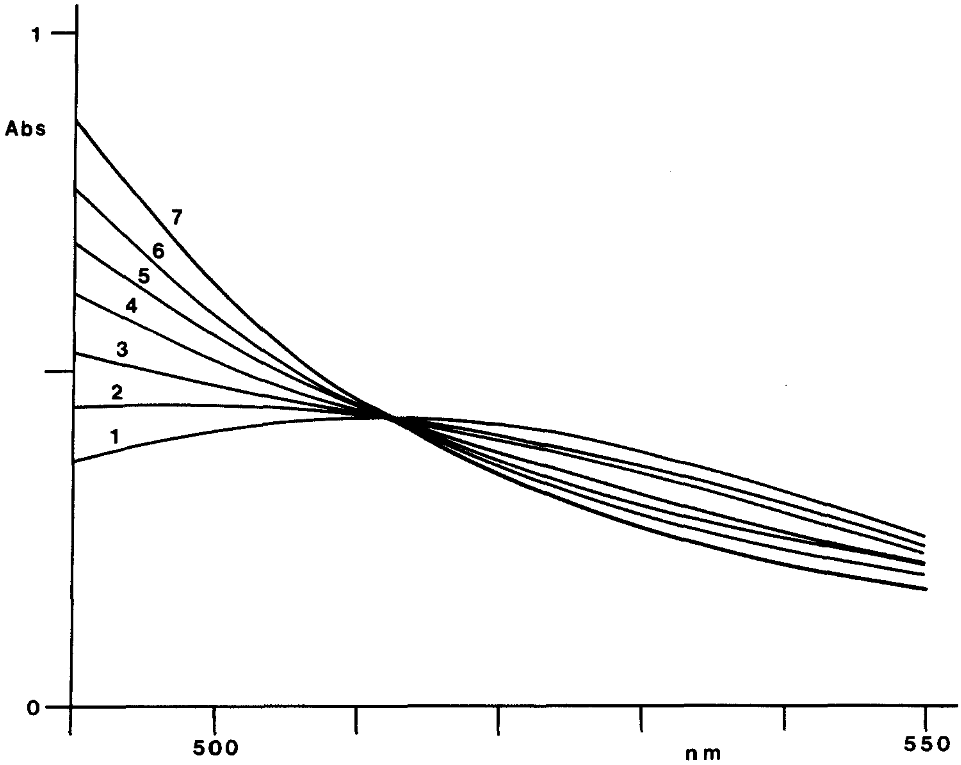


FIGURE 4 Visible spectra at 283 K in 1 cm cell of $CHCl_3$ solutions containing constant amounts of I_2 (4.8×10^{-4}) and variable Ph_4todit concentrations in the ratios: 1 = 1:0, 2 = 1:0.5, 3 = 1:1, 4 = 1:2, 5 = 1:3, 6 = 1:5, 7 = 1:10.

The principal i.r. bands are listed in the experimental part. However, as previously observed in similar cases, conclusive evidence can not be obtained from i.r. spectral results alone since only small shifts of the ligand bands are observed in the diiodine complexes and vibrational coupling effects cause difficulties in the assignments of C=S bands.[7,8]

The F.T. Raman spectrum in the region below 300 cm^{-1} shows a strong band at 172 cm^{-1}, a weak doublet at 145–135 cm^{-1} and a band of medium intensity at 114 cm^{-1}. Raman spectroscopy, substantiating X-ray data, has shown to be a valuable means in studying diiodine complexes.[9] In fact the strong Raman band at 205 cm^{-1} due to I—I vibration in free diiodine is expected to decrease as a consequence of the lengthening of the I—I distance on coordination to donors (in the donor-acceptor complex the highest occupied molecular orbital has I—I antibonding character). In particular it is well established that unsymmetrical I_3^- gives rise to a strong band in the 99–116 cm^{-1} region and to a relatively weak second band in the 130–150 cm^{-1} region (these bands can be split for solid state reasons). We attribute the band found at 172 cm^{-1} in Ph_4todit · $2I_2$ · $2CHCl_3$ to the diiodine stretching frequency in the complex, while the other Raman bands observed in this region are probably due to some I_3^- formed on decomposition.

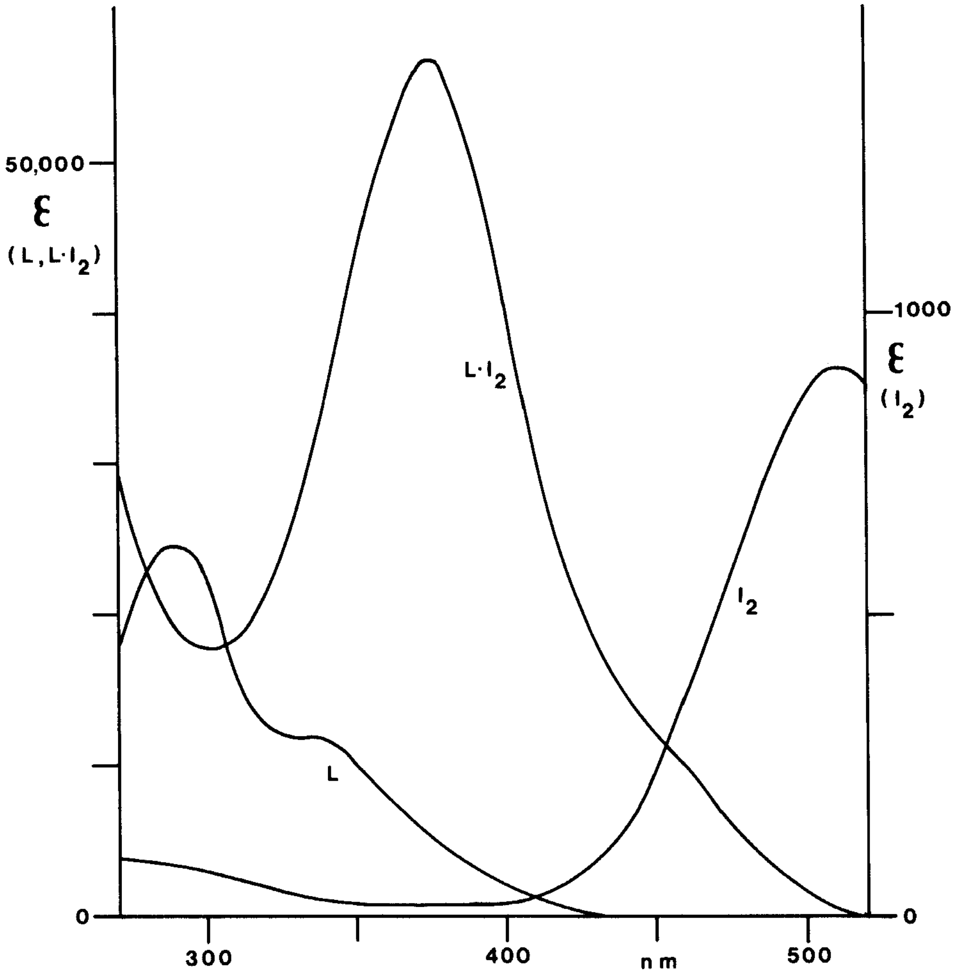


FIGURE 5 Calculated u.v-visible spectra of the 1:1 complex between Ph_4todit(L) and I_2 at 283 K in $CHCl_3$ solutions. Spectra of the free reagents are reported for comparison.

TABLE III

Logarithms of the equilibrium constants, enthalpy (Kcal mol^{-1}) and entropy changes (cal K^{-1} mol^{-1}) for the formation of 1:1 complex between I_2 and Ph_4todit in $CHCl_3$ solutions. The values for the Et_4todit case are reported for comparison (see Ref. 5)

T°C	log K (Ph_4todit)	log K (Et_4todit)
35	2.499	2.648(9)
30	2.524	
25	2.569	2.777(8)
20	2.637	2.786(7)
15	2.698	2.858(6)
10	2.732	2.937(7)

$\Delta H° = -3.9(2)$ Kcal mol^{-1}, $\Delta H° = -4.4(5)$ Kcal mol^{-1},
$\Delta S° = -1(1)$ cal K^{-1} mol^{-1}, $\Delta S° = -2(2)$ cal K^{-1} mol^{-1}.

A comparison with the corresponding Et$_4$todit case shows: i) the formation constants of the 1:1 complex are a little lower, ii) the value of the enthalpy of formation is very similar, iii) the I—I vibration falls at higher frequencies. In fact the band attibuted to I—I vibration falls at 147 cm^{-1} in Et$_4$todit · 2I$_2$. We conclude that the Raman measurements are the most sensitive to show unambigously even small differences in the relative donor strength. The difference of the I—I vibrations in the two complexes ($\Delta\nu$ = 25 cm^{-1}) indicates that the lengthening of I—I distance for Et$_4$todit is more pronounced as a consequence of a higher donation of this ligand with respect to Ph$_4$todit. That can be due to an electron withdrawing effect by Ph groups which reduces the capability of the π-electron flow from the N-atom to the S through the system N—C—S. The steric-hindrance of substituents should be less important in affecting the S-donation. In fact, in the hypothesis that I$_2$ is similarly coordinated to thionic sulphur as in the cases until now reported, the expected almost linear arrangement of S—I—I with an angle of C—S—I near to 90° should not be affected by the steric hindrance of N-substituents.

EXPERIMENTAL

Synthesis. The Ph$_4$todit compound has been prepared as previously described.[1] Well formed crystals of Ph$_4$todit · CHCl$_3$ suitable for X-ray analysis have been obtained by slow evaporation of a CHCl$_3$ solution. When mixed with I$_2$ in CHCl$_3$, in ratios varying between 1:2 up to 1:10 (Ligand to I$_2$) the analytical and spectroscopic results on the solid obtained by evaporation, are always the same according to the formulation Ph$_4$todit · 2I$_2$ · 2CHCl$_3$. The solid is obtained in the form of lustrous red-brown microcrystals. The presence of CHCl$_3$ is confirmed by i.r. results.
Analytical results: Found: C 27.59 H 1.30 N 4.21 S 14.50
Calc. for $C_{32}H_{22}Cl_6I_4N_4S_6$: C 27.98 H 1.61 N 4.07 S 13.99

Spectroscopic measurements. I.r. spectra (cm^{-1}) were recorded on a Perkin Elmer mod 983 Spectrophotometer as KBr pellets: 3059w 3039w 1590m 1490s 1452mw 1391s 1372sh 1330vs 1308s 1213w 1170w 1160w 1073m 1023m 1004m 989w 918m 839w 778m 751vs 696sh 688s 618w 608m 518m.

Raman spectra have been recorded by courtesy of Bruker Company (Milano), on IFS.66 Instrument using an exciting line of wavenumber 9394 cm^{-1} of a Nd:YAG-Laser.

The electronic spectra were measured at different temperatures (±0.1°C) in the range of 10–35°C in 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 (4.8 $\times$ 10^{-4} mol dm^{-3}) and variable Ph$_4$todit concentrations, ranging from 1.2 $\times$ 10^{-4} to 4.8 $\times$ 10^{-4} mol dm^{-3} (see Figure 4) was prepared and the spectra recorded between 450 and 550 nm using 1 cm silica cells. Another set of solutions was prepared with a constant concentration of Ph$_4$todit (4.8 $\times$ 10^{-4} mol dm^{-3}) and variable diiodine concentrations ranging from 4.8 $\times$ 10^{-4} to 9.6 $\times$ 10^{-3} mol dm^{-3} in 1 mm silica cells, in the 260–450 nm range (Figure 3).

Calculations. The experimental points used in the calculations have been taken from the recorded spectra at 10 nm intervals and the total number was always 130 readings for each system at each temperature. A general computer program, derived from "SUPERSQUAD"[10] has been used to refine simultaneously equilibrium constants and molar extinction coefficients from the spectrophotometric data.

Structure determination. The cell parameters were determined by least-squares refinement from the Θ values of 27 reflections accurately measured. All diffraction measurements were made on a Siemens AED diffractometer using the Ni-filtered Cu-kα radiation. Observations were collected by $\Theta/2\Theta$ scan (with Θ in the range 3–70°) giving 6427 measurements of which 2958 having $I \geq 2\sigma(I)$ were considered observed and used in the analysis. The space group was $P2_1/n$. Intensity data were corrected for the Lorentz-polarization factor, for absorption (maximum and minimum values 1.16802, 0.82947) and extinction (maximum and minimum values 1.11360, 0.96377) following the empirical method of Walker and Stuart.[11] The structure was solved by Patterson and Fourier methods and refined by block-matrix least-squares,[12] with anisotropic thermal parameters for all the non-hydrogen atoms, excluding those of the phenyl groups. The hydrogen atoms were located from a ΔF map and their coordinates were introduced in the final structure factor calculation. Convergence was reached at R = 0.0551. Crystal Data. $C_{31}H_{21}Cl_3N_4S_6$, $M = 748.253$. Monoclinic, space group $P2_1/n$, $a = 13.393(5)$, $b = 20.764(6)$, $c = 12.286(5)$ Å, $\beta = 97.88(2)°$, $V = 3384(2)$ Å^3, $Z = 4$, μ[Cu-kα] = 61.62 cm^{-1}, $F(000) = 1528$, $\lambda = 1.541838$ Å.

Compound: 4,5,6,7-tetrathiocino[1,2-b:3,4-b′] diimidazolyl-1,2,8,10-tetraphenyl-2,9-dithione

Experimental data for the crystallographic analyses

Formula	$C_{31}H_{21}Cl_3N_4S_6$
M	748.253
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.393(5)
b/Å	20.764(6)
c/Å	12.286(5)
β/°	97.88(2)
V/Å^3	3384(2)
Z	4
Dc/Mg m^{-3}	1.469
Dobs/Mg m^{-3}	1.48
$F(000)$	1528
Temperature/K	295
Crystal size/mm^3	0.06 × 0.09 × 0.43
Diffractometer	Siemens AED
μ/cm^{-1}	61.62
Scan type	$\theta/2\theta$
Scan speed	0.20–0.10–0.05
Scan width	1.20 + 0.142 tgθ
Radiation	Ni-filtered CuKα
Wavelength/Å ($\bar{\lambda}$)	1.541838
θ-range	3–70
Reflections for lattice parameters	number 27 θ-range 20–34
Std reflcn measured after every 50	−6 11 1
h-range	−16 16
k-range	0 25
l-range	0 14
No. of meas. refl.	6427
Condition for obs.	$I \geqslant 2\sigma(I)$
No. reflections used in the refinement	2958
Absorption correction	min. 0.82947 max 1.16802
Extinction correction	min. 0.96377 max. 1.11360
Min., max. height in final ΔF map (eÅ^{-3})	−0.44 0.39
$R = \Sigma \mid \Delta F \mid / \Sigma \mid F_0 \mid$	0.0551
$R_w = [\Sigma w(\Delta F)^2 / \Sigma w F_0^2]^{1/2}$	0.0680
k, g ($w = K/[\sigma^2(F_0) + gF_0^2]$)	0.4921 0.005337

Note. The tables of experimental data for the crystallographic analysis, of bond-distances and bond-angles, and of anisotropic or isotropic thermal parameters are deposited with the Cambridge Crystallographic Data Center (CCDC), U.K.

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REFERENCES

1. F. Bigoli, M. A. Pellinghelli, D. Atzei, P. Deplano and E. F. Trogu, *Phosphorus and Sulfur*, **37**, 189 (1988).
2. F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Inorg. Chim. Acta*, **180**, 201 (1991).
3. F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chim. Acta*, **182**, 33 (1991).
4. F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chim. Acta*, **170**, 245 (1990).
5. D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem.*, **67**, 1416 (1989).
6. C. N. R. Rao and A. S. N. Murthy, "Spectroscopy of Donor-Acceptor System," chapter of "Spectroscopy in Inorganic Chemistry," Ed. Rao and Ferraro, Academic Press, Vol. I, p. 117 (1970).
7. H. E. Hallam and C. M. Jones, *Spect. Chim. Acta*, **25A**, 1791 (1969).
8. K. Dwarakanath and D. N. Sathyanarayana, *Bull. Chem. Soc. Japn.*, **52**, 2699 (1979).
9. T. J. Marks, *Ann. N.Y. Ac. Sci.*, 594 (1978).
10. P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1195 (1985).
11. N. Walker and D. Stuart, *Acta Crystallogr.*, Sect. A, 39 (1983) 158. The program ABSORB was used (F. Ugozzoli, *Comput. Chem.*, **11**, 109 (1987).
12. G. Sheldrick, SHELX 76, A program for Crystal Structure Determination, University of Cambridge (1976).