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Spectroscopic Studies and X-Ray Crystal Structures of Charge-Transfer Complexes of 1,4,7-Trithiacyclononane with Diiodine

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ABSTRACT

1,4,7-Trithiacyclononane ($[9]aneS_3$) *reacts with molecular diiodine in* CH_2Cl_2 *to form a 1:1 adduct. The formation constant and the thermodynamic parameters of this adduct have been determined by UV-visible spectra of several solutions at the temperatures of 15, 20, 25, 30, and 35°C. The* ^{13}C *NMR spectra show that adducts with higher ligand/diiodine molar ratios are formed. Two neutral charge-transfer molecular compounds having formula* $2[9]aneS_3 \cdot 4I_2$ (**I**) *and* $[9]aneS_3 \cdot 3I_2 \cdot$ (**II**) *have been obtained as crystals. The crystals of* **I** *are triclinic* ($a = 8.498(2)$ Å, $b = 13.984(4)$ Å, $c = 14.898(6)$ Å, $\alpha = 65.57(2)°$, $\beta = 89.19(2)°$, $\gamma = 81.26(2)°$, $Z = 2$, *space group* $P\bar{1}$; $R = 0.025$) *and contain units formed by two* $[9]aneS_3$ *molecules connected by a diiodine molecule; one* $[9]aneS_3$ *binds two other diiodine molecules, while the second binds only one other diiodine molecule. The crystals of* **II** *are monoclinic* ($a = 13.810(2)$ Å, $b = 9.829(4)$ Å, $c = 16.198(6)$ Å, $\beta = 113.41(2)°$, $Z = 4$, *space group* $P2_1/c$; $R = 0.019$) *and contain molecules of* $[9]aneS_3$ *binding three diiodine molecules. FT-Raman spectra in the characteristic* $\nu(I-I)$ *region, carried out on the solid adducts, are discussed in comparison with the structural parameters.*

INTRODUCTION

For several years [1–6], the interaction between diiodine and numerous donors (D), all containing at least one thio- or seleno-amido group, have been investigated in CH_2Cl_2 solution by UV-VIS spectroscopy, according to the equilibrium reaction

$$D + I_2 \rightleftharpoons DI_2 \qquad (1)$$

The main purpose was to measure the influence of the chemical environment on the donor properties of the chalcogen atom by determining the formation constants (K) and the thermodynamic parameters of Reaction 1. This type of research was first stimulated by the interest in the molecular adducts formed between antithyroid drugs and diiodine in the study of hyperthyroidism [7].

More recently, many articles have been reported [8–10] about electric properties of solid polyiodide salts obtained by reacting diiodine with compounds having sulfur or selenium donor atoms. This has led to an extension of the study to the solid state, using the same substrates employed for the studies in solution.

Until now, we have found that neutral charge-transfer complexes [11] with stoichiometries different from the one in solution (1:1 adduct) can be obtained in the solid state. In two cases, i.e., with N-methylbenzothiazole-2-thione and -2-selone, we

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TABLE 1 Crystallographic Data

	2[9]aneS₃·4I₂(I)	*[9]aneS₃·3I₂(II)*
Formula	$C_{12}H_{24}I_8S_6$	$C_6H_{12}I_6S_3$
F.w. (amu)	1375.94	941.78
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.498(2)	13.810(2)
b (Å)	13.984(4)	9.829(4)
c (Å)	14.898(6)	16.198(6)
α (°)	65.57(2)	90
β (°)	89.19(2)	113.41(2)
γ (°)	81.26(2)	90
V (Å^3)	1591(1)	2018(1)
Z	2	4
D_{calcd} (g cm^{-3})	2.872	3.100
Crystal dimensions (mm)	0.18 × 0.15 × 0.12	0.13 × 0.14 × 0.10
μ (Mo*K*α) (cm^{-1})	81.03	94.24
Transmission factors:		
Psi-scan	0.74–1.00	
Difabs	0.81–1.20	0.75–1.23
Scan mode	ω	ω
ω-Scan width (°)	1.0 + 0.35 tan θ	0.80 + 0.35 tan θ
θ-Range (°)	3–25	3—20
Octants of reciprocal Space explored	±h, +k, ±l	+h, +k, ±l
Measured reflections	5572	1976
Unique reflection with $I > 3\sigma(I)$	4888	837
Final R and R_w indices[a]	0.025, 0.044	0.019, 0.023
Number of variables	236	137
GOF[b]	1.819	1.176

[a] $R = [\Sigma(F_0 - k\,|F_c|)/\Sigma F_0]$ $\quad R_w = [\Sigma w(F_0 - k\,|F_c|)^2/\Sigma w F_0^2]^{1/2}$.
[b] $\mathrm{GOF} = [\Sigma w(F_0 - k\,|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$.

have obtained iodonium salts having polyiodides [12] as counter ions. The latter two compounds, which have interesting structural features, have proven to be poor electric conductors [12].

The FT-Raman spectra, recorded on all the structurally characterized compounds in order to check the ability of Raman spectroscopy to identify the nature of iodine [13–19], have shown that this technique alone is inadequate to distinguish unambiguously each type of polyiodide and the polyiodides from the neutral adducts [20]. Raman spectroscopy can only give valuable information on the extent of the lengthening of the I–I bond induced by the donor. Some polyiodides show FT-Raman spectra indistinguishable from those displayed by neutral complexes of weak or medium strength; in such cases, the polyiodide can be regarded as a diiodine molecule perturbed by an I_n^- (n = 1, 3, ...) donor.

With the objective of extending this research to a new class of compounds containing sulfur or selenium donor atoms, we have considered cyclic thioether ligands. Mesocyclic and macrocyclic polythioethers have been found to be effective polydentate ligands for complexing a variety of transition metal ions, in spite of their moderately low σ-donor and π-acceptor abilities. In recent years, these complexes have generated great interest by their similarity to biological systems and their unusual kinetic and thermodynamic properties [21–24].

In this article, we report the results of the UV-VIS and ^{13}C NMR spectroscopic studies of the equilibria between I_2 and [9]aneS$_3$ in CH_2Cl_2 solution, and we have determined X-ray crystal structures of the two complexes 2[9]aneS$_3$·4I$_2$ (**I**) and [9]aneS$_3$·3I$_2$ (**II**). Furthermore, FT-Raman spectra recorded for **I** and **II** are discussed in consideration of the structural features.

*EXPERIMENTAL**

Materials

Diiodine was purified by sublimation from KI and stored in a desiccator. [9]aneS$_3$ was purchased from Aldrich and purified by sublimation to obtain analytic purity.

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*Supplementary materials are available from the Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

TABLE 2 Fractional Atomic Coordinates wih Esd's for 2[9]aneS$_3$ · 4I$_2$(**I**)

Atom	*x*	*y*	*z*
I(1)	1.21829(4)	1.01619(2)	−0.07724(2)
I(2)	1.23237(5)	1.20861(3)	−0.24281(3)
I(3)	0.80914(5)	0.44872(3)	0.12855(3)
I(4)	0.53579(4)	0.36295(3)	0.13487(3)
I(5)	1.68332(4)	0.48925(3)	0.39885(3)
I(6)	1.95338(5)	0.35311(3)	0.50731(3)
I(7)	−0.31480(5)	0.15701(3)	0.41542(3)
I(8)	−0.55550(6)	0.18492(5)	0.53598(4)
S(1)	1.1980(2)	0.81788(9)	0.07494(9)
S(2)	1.1245(2)	0.55034(9)	0.1351(1)
S(3)	1.4010(2)	0.6254(1)	0.2844(1)
S(4)	0.1712(2)	−0.0009(1)	0.1838(1)
S(5)	0.2643(2)	0.2288(1)	0.1758(1)
S(6)	−0.0605(2)	0.1352(1)	0.2922(1)
C(1)	1.1189(7)	0.7622(4)	−0.0031(4)
C(2)	1.0169(6)	0.6790(4)	0.0514(4)
C(3)	1.1181(7)	0.5550(5)	0.2558(4)
C(4)	1.2837(7)	0.5211(5)	0.3102(4)
C(5)	1.4621(6)	0.6535(4)	0.1596(4)
C(6)	1.4110(7)	0.7691(5)	0.0889(5)
C(7)	0.3715(7)	0.0268(5)	0.1857(4)
C(8)	0.4006(6)	0.1029(4)	0.2294(4)
C(9)	0.1912(7)	0.2454(4)	0.2854(5)
C(10)	0.1015(7)	0.1597(4)	0.3527(4)
C(11)	−0.0270(7)	−0.0091(4)	0.3372(4)
C(12)	0.1327(8)	−0.0575(4)	0.3143(4)

The compound with a [9]aneS$_3$/diiodine ratio of 1:1 was obtained as a powder by evaporating a CH_2Cl_2 solution of reagents in the same molar ratio in air and at room temperature. Elem. Anal.: (calcd for $C_6H_{12}S_3I_2$) found: C (16.6) 16.8; H (2.8) 2.7; S (22.1) 22.1%.

2[9]aneS$_3$ · 4I$_2$ (**I**)

This compound was obtained by slow diffusion of *n*-hexane into a carbon tetrachloride solution of [9]aneS$_3$ and diiodine in a 1:1 molar ratio and slow evaporation of the solution so obtained in air and at room temperature. After several days, brown crystals with a violet metallic luster were formed.

Elem. Anal.: (calcd for $C_6H_{12}S_3I_4$) found: C (10.5) 10.5; H (1.8) 1.7; S (16.0) 13.9%.

[9]aneS$_3$ · 3I$_2$ (**II**)

This compound was obtained by allowing a carbon tetrachloride solution of [9]aneS$_3$ and diiodine in a 1:3 molar ratio to stand in air and at room temperature. After 2 days, brown needle-shaped crystals with a violet metallic luster were formed.

Elem. Anal.: (calcd for $C_6H_{12}S_3I_6$) found: C (7.7) 7.9; H (1.3) 1.3; S (10.2) 10.4%.

TABLE 3 Fractional Atomic Coordinates with Esd's for [9]aneS$_3$ · 3I$_2$ (**II**)

Atom	*x*	*y*	*z*
I(1)	0.04426(5)	0.6551(2)	0.17970(4)
I(2)	−0.08748(5)	0.6777(2)	−0.00086(4)
I(3)	0.43966(5)	1.1174(2)	0.61123(4)
I(4)	0.56122(5)	1.3513(2)	0.64897(5)
I(5)	0.26727(5)	0.3446(2)	0.71855(4)
I(6)	0.28307(6)	0.1833(2)	0.86215(4)
S(1)	0.1770(2)	0.6641(6)	0.3689(1)
S(2)	0.3004(2)	0.8879(7)	0.5597(2)
S(3)	0.2689(2)	0.5035(7)	0.5658(1)
C(1)	0.1580(8)	0.843(2)	0.3805(6)
C(2)	0.2604(8)	0.918(2)	0.4396(6)
C(3)	0.3888(7)	0.741(2)	0.5871(6)
C(4)	0.3566(7)	0.631(2)	0.6362(6)
C(5)	0.1413(7)	0.585(2)	0.5198(5)
C(6)	0.0939(6)	0.583(2)	0.4172(5)

TABLE 4 Molar Extinction Coefficients (ϵ) at the Wavelengths (λ) Used for the Calculation, Formation Constants (*K*), Ranges of the Saturation Fraction (*s*), and Sum of the Squared Deviations (χ^2) for 1:1 Molecular Adduct between Diiodine and [9]aneS$_3$ (Standard Deviations in Parentheses).

t (°C)	λ (*nm*)	ϵ ($cm^2\ mol^{-1}$)	*K* ($dm^3\ mol^{-1}$)	*s*	χ^2
15	310	26460(210)	275(7)	0.45 ÷ 0.87	0.10
	340	16040(110)			
	360	6780(53)			
	380	3030(34)			
	400	2610(21)			
	420	2780(20)			
20	310	25980(220)	220(6)	0.39 ÷ 0.84	0.10
	340	15800(118)			
	360	6770(57)			
	380	3040(37)			
	400	2560(23)			
	420	2720(21)			
25	310	26170(195)	169(4)	0.33 ÷ 0.81	0.07
	340	15800(125)			
	360	6870(58)			
	380	3100(37)			
	400	2550(23)			
	420	2690(22)			
30	310	25710(196)	137(3)	0.29 ÷ 0.77	0.06
	340	15560(126)			
	360	6870(60)			
	380	3110(39)			
	400	2510(24)			
	420	2630(22)			
35	310	25310(195)	110(3)	0.25 ÷ 0.73	0.05
	340	15380(129)			
	360	6880(63)			
	380	3120(44)			
	400	2480(24)			
	420	2580(22)			

$\Delta H = -34 \pm 1$ (K joule · mol^{-1}) $r^a = 1.000$

$\Delta S = -71 \pm 2$ (joule · deg^{-1})

[a] Correlation coefficient of the Arrhenius plot ln *k vs.* $1/T°$.

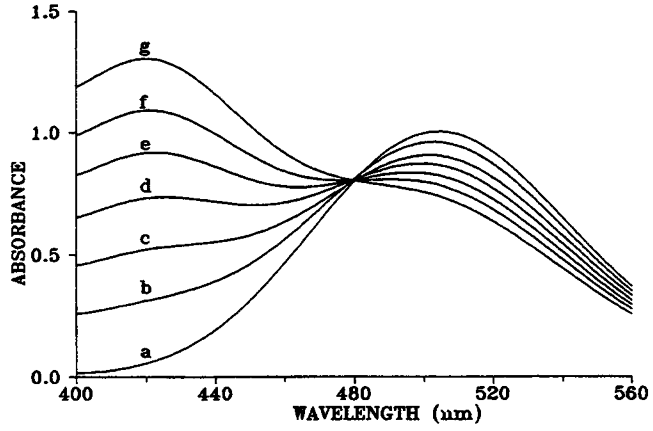

FIGURE 1 Isosbestic point obtained between the visible band of the free diiodine and its blue shifted band. $[I_2] = 1.06 \cdot 10^{-3}$ M and $[[9]aneS_3] = 0.0, 5.034 \cdot 10^{-4}, 1.007 \cdot 10^{-3}, 1.515 \cdot 10^{-3}, 2.014 \cdot 10^{-3}, 2.517 \cdot 10^{-3}$ and $3.272 \cdot 10^{-3}$ M for a, b, c, d, e, f and g, respectively.

X-Ray Diffraction Data Collection and Structure Determination

Crystal data and other experimental details are summarized in Table 1. The crystals used were coated with cyanoacrylate glue in order to prevent loss of diiodine during data collection. The diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). A least-squares fit of 25 randomly oriented intense reflections having $8° < \theta < 18°$ provided the unit cell parameters and an orientation matrix. The diffracted intensities were collected using a variable scan speed. Three standard reflections were measured at regular intervals and showed a constant decay of the scattering power of the crystal, which was evaluated at about 8 and 50% on F_0 for **I** and **II** respectively. The two sets of data were therefore corrected for decay as well as for Lorentz and polarization effects. An absorption correction was applied to the data obtained for **I**, according to the procedure described in Demartin *et al.* [25], i.e., by performing a psi-scan correction [26] followed by a DIFABS correction [27]; for compound **II**, owing to the quick decay of the crystal, only the DIFABS correction could be applied. Secondary extinction correction was in the form $|F_0|/(1 + gIc)$ with $g = 3.4 \times 10^{-7}$ and 3.5×10^{-8} for **I** and **II**, respectively. Scattering factors for all the atomic species and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from Ref. [28]. Both structures were solved by direct methods (MULTAN) [29] and refined by full-matrix least squares, minimizing the function $\Sigma w(|F_0| - k|F_c|)^2$.

Individual weights were assigned as $w = 1/\sigma^2(F_0)$, where $\sigma(F_0) = \sigma(F_0^2)/2F_0$, $\sigma(F_0^2) = [\sigma^2(I) +$

TABLE 5 Selected Interatomic Distances (Å), Angles (Degrees), and Torsion Angles (Degrees) within the $[9]aneS_3$ Rings

	$2[9]aneS_3 \cdot 4I_2$ (*I*)	$[9]aneS_3 \cdot 3I_2$ (*II*)
I(1)-I(2)	2.818(1)	2.772(1)
I(3)-I(4)	2.755(1)	2.768(2)
I(5)-I(6)	2.781(1)	2.751(2)
I(7)-I(8)	2.792(1)	
I(1) ... I(1) I	4.321(1)	
I(2) ... I(6) II	4.017(1)	
I(2) ... I(8) III	3.844(1)	
I(3) ... I(5) IV	4.389(1)	
I(4) ... I(4) V	4.223(1)	
I(4) ... I(7) VI	4.057(1)	
I(6) ... I(7) VII	4.436(1)	
I(2) ... I(2) VIII		4.241(3)
I(2) ... I(5) IX		3.786(1)
I(2) ... I(6) X		4.363(1)
I(3) ... I(5) XI		4.119(2)
I(3) ... I(6) XII		4.226(2)
I(4) ... I(6) XIII		3.951(3)
I(1)-S(1)	2.792(1)	2.880(3)
I(3)-S(2)	3.239(1)	2.865(6)
I(4)-S(5)	3.089(1)	
I(5)-S(3)	2.887(1)	2.933(4)
I(7)-S(6)	2.878(1)	
S(1)-C(1)	1.828(4)	1.80(3)
C(1)-C(2)	1.506(6)	1.54(2)
C(2)-S(2)	1.818(4)	1.82(1)
S(2)-C(3)	1.826(5)	1.82(2)
C(3)-C(4)	1.541(6)	1.52(3)
C(4)-S(3)	1.799(5)	1.80(2)
S(3)-C(5)	1.821(5)	1.81(1)
C(5)-C(6)	1.517(6)	1.53(1)
C(6)-S(1)	1.818(4)	1.81(1)
S(4)-C(7)	1.805(5)	
C(7)-C(8)	1.509(6)	
C(8)-S(5)	1.823(4)	
S(5)-C(9)	1.829(5)	
C(9)-C(10)	1.511(6)	
C(10)-S(6)	1.805(4)	
S(6)-C(11)	1.821(4)	
C(11)-C(12)	1.521(7)	
C(12)-S(4)	1.817(5)	
S(1)-I(1)-I(2)	174.83(2)	173.5(2)
S(2)-I(3)-I(4)	176.14(2)	175.1(1)
S(3)-I(5)-I(6)	178.20(2)	174.5(1)
S(5)-I(4)-I(3)	168.86(2)	
S(6)-I(7)-I(8)	177.53(3)	
C(1)-S(1)-I(1)	95.9(1)	94.8(5)
C(6)-S(1)-I(1)	95.5(2)	101.7(3)
C(2)-S(2)-I(3)	88.2(1)	93.9(6)
C(3)-S(2)-I(3)	102.3(2)	104.1(6)
C(4)-S(3)-I(5)	96.0(2)	93.7(5)
C(5)-S(3)-I(5)	100.8(1)	104.6(4)
C(8)-S(5)-I(4)	93.3(1)	
C(9)-S(5)-I(4)	98.4(2)	
C(10)-S(6)-I(7)	99.8(2)	
C(11)-S(6)-I(7)	98.6(2)	
S(1)-C(1)-C(2)	112.9(3)	113.3(13)
C(1)-C(2)-S(2)	115.5(3)	113.5(11)
C(2)-S(2)-C(3)	104.3(2)	106.0(7)
S(2)-C(3)-C(4)	112.4(3)	112.8(9)

TABLE 5 Continued

	$2[9]aneS_3 \cdot 4I_2$ (*I*)	$[9]aneS_3 \cdot 3I_2$ (*II*)
C(3)-C(4)-S(3)	115.9(3)	115.6(8)
C(4)-S(3)-C(5)	103.5(2)	104.8(9)
S(3)-C(5)-C(6)	112.6(3)	111.6(8)
C(5)-C(6)-S(1)	116.0(3)	113.1(8)
C(6)-S(1)-C(1)	104.7(2)	104.1(8
S(4)-C(7)-C(8)	117.8(3)	
C(7)-C(8)-S(5)	112.6(3)	
C(8)-S(5)-C(9)	102.3(2)	
S(5)-C(9)-C(10)	115.3(3)	
C(9)-C(10)-S(6)	114.7(3)	
C(10)-S(6)-C(11)	103.1(2)	
S(6)-C(11)-C(12)	115.4(3)	
C(11)-C(12)-S(4)	113.3(3)	
C(12)-S(4)-C(7)	102.1(2)	
S(1)-C(1)-C(2)-S(2)	−75.1	−78.3
C(1)-C(2)-S(2)-C(3)	96.6	91.1
C(2)-S(2)-C(3)-C(4)	−130.3	−128.5
S(2)-C(3)-C(4)-S(3)	87.9	91.6
C(3)-C(4)-S(3)-C(5)	−72.5	−76.6
C(4)-S(3)-C(5)-C(6)	122.8	121.0
S(3)-C(5)-C(6)-S(1)	−59.1	−55.2
C(5)-C(6)-S(1)-C(1)	−75.9	−78.1
C(6)-S(1)-C(1)-C(2)	111.0	120.0
S(4)-C(7)-C(8)-S(5)	−52.3	
C(7)-C(8)-S(5)-C(9)	130.6	
C(8)-S(5)-C(9)-C(10)	−61.7	
S(5)-C(9)-C(10)-S(6)	−52.8	
C(9)-C(10)-S(6)-C(11)	131.8	
C(10)-S(6)-C(11)-C(12)	−59.3	
S(6)-C(11)-C(12)-S(4)	−54.4	
C(11)-C(12)-S(4)-C(7)	131.9	
C(12)-S(4)-C(7)-C(8)	−60.3	

Symmetry codes:
(I) $2 - x, 2 - y, -z$; (II) $x - 1, 1 + y, z - 1$; (III) $2 + x, 1 + y, z - 1$; (IV) $x - 1, y, z$; (V) $1 - x, 1 - y, -z$; (VI) $1 + x, y, z$; (VII) $2 + x, y, z$; (VIII) $-x, 1 - y, -z$; (IX) $-x, 1/2 + y, 1/2 - z$; (X) $-x, 1 - y, 1 - z$; (XI) $x, 1 + y, z$; (XII) $x, 3/2 - y, z - 1/2$; and (XIII) $1 - x, 3/2 + y, 3/2 - z$.

$(pI)^2]^{1/2}/\mathrm{LP}$, and p, the "ignorance factor," is equal to 0.04 and 0.03 for **I** and **II** respectively.

Anisotropic thermal parameters were assigned to all the nonhydrogen atoms. The hydrogen atoms were introduced in the structure model with an imposed thermal parameter at calculated positions (C-H 0.95 Å); no refinement was attempted for these atoms. The final Fourier difference synthesis showed maxima residuals of 1.2 and 0.5 e/Å^3 close to the iodine atoms for **I** and **II** respectively. The final atomic coordinates are listed in Tables 2 and 3. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package [30].

FT-Raman Spectra

The FT Raman spectra were recorded on an FRA 106 FT Raman accessory mounted on a Bruker IFS 66 FT-IR vacuum instrument operating with an exciting frequency of 1064 nm (Nd:YAG laser). No sample decomposition was observed during the experiments.

^{13}C NMR Measurements

The studies were carried out in methylene chloride solutions. The spectra of several solutions having the same concentration of $[9]aneS_3$ with increasing amounts of diiodine were recorded. Likewise, the maximum diiodine/donor molar ratio employed was 3.5 in order to shift the equilibrium reaction toward complex formation.

The ^{13}C NMR spectra were recorded at the temperature of 20°C on a Varian FT-NMR spectrometer VXR 300, operating at 75.4 MHz frequency. $CDCl_3$ (77.00 ppm) was employed as the external reference.

Spectrophotometric Measurements and Data Treatment

The spectrophotometric measurements in CH_2Cl_2 solutions were carried out by use of a Varian model Cary 5 UV-Vis-NIR spectrophotometer having a temperature controller accessory and connected with an IBM Personal System 2 Type 8513 TKQ S/N 55-DMR89. The spectra of 13 different solutions were recorded in the 300–500 nm range at temperatures of 15, 20, 25, 30, and 35°C. The choice of the concentrations of the reagents was made according to the criteria outlined in Ref. [31] and widely discussed in previous articles [4,5]; however, in all the solutions, the concentration of $[9]aneS_3$ was always higher than that of diiodine in order to avoid the formation of adducts different from 1:1. Data analysis was carried out with a program based on a nonlinear least-squares method [32] based on the assumption that the best values of K and ϵ are those which minimize the sum of the function $\chi^2 = \Sigma(A_c - A_s)^2/(N - 2)$, where A_c and A_s are the calculated and experimental absorbances and N is the number of data points. The optimization of K was carried out on six different wavelengths.

RESULTS AND DISCUSSION

$[9]aneS_3$ has three sulfur atoms able to bind molecular diiodine, and 1:1, 1:2, and 1:3 molecular complexes are to be expected. In the conditions of the experimental spectrophotometric measurements, only the formation of the 1:1 adduct is important, as verified by the presence of the isosbestic point at 480 nm, which is found also for $[I_2] > [[9]aneS_3]$ (Figure 1).

However, in order to avoid any formation of complexes different from 1:1, all the solutions used for the calculation of the stability constants of Reaction 1 were prepared with an excess of $[9]aneS_3$. The K values, optimized using the absorbance values at six different wavelengths, and the ϵ values at the same wavelengths are collected in Table 4, together with the ranges of the saturation fraction

TABLE 6 Geometrical Parameters for the Interaction of the Thioether Sulfur with Diiodine S···I(1)-I(2)

Compound	*d*[S···*I*(*1*)] (*Å*)	*d*[*I*(*1*)-*I*(*2*)] (*Å*)	<*S*···*I*(*1*)-*I*(*2*) (°)	*Reference*
2[9]aneS$_3$ · 4I$_2$ (**I**)	2.792(1)	2.818(1)	174.83(2)	this work
	2.887(1)	2.781(1)	178.20(2)	
	3.089(1)[a]	2.755(1)[a]	168.86(2)[a]	
	2.878(1)	2.792(1)	177.53(3)	
[9]aneS$_3$ · 3I$_2$ (**II**)	2.880(3)	2.772(1)	173.5(2)	this work
	2.865(6)	2.768(2)	175.1(1)	
	2.933(4)	2.751(2)	174.5(1)	
1,4-Dithiane · 2I$_2$	2.867(6)	2.787(2)	177.9(4)	36
Dithia[3.3.1]propellane · 2I$_2$	2.852(2)	2.797(1)		37
	2.806(2)	2.796(1)		
Dithia[3.3.2]propellane · 2I$_2$	2.803(2)	2.794(1)		37
	2.902(2)	2.767(1)		
2(C$_{12}$H$_{24}$O$_4$S$_2$) · 5I$_2$[b]	2.848(3)	2.775(2)	173.47(7)	38
	2.774(3)	2.821(2)	175.24(6)	
	2.761(3)	2.810(2)	178.03(6)	
	2.654(3)	2.902(2)	175.97(7)	
Benzylsulphide · I$_2$	2.78	2.819	179	38

[a] These values are with regard to the I-I bridged between two sulfur atoms; the reported S···I distance is the shorter one.
[b] 2(C$_{12}$H$_{24}$O$_4$S$_2$) · 5I$_2$ = 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecanebis(diiodine).

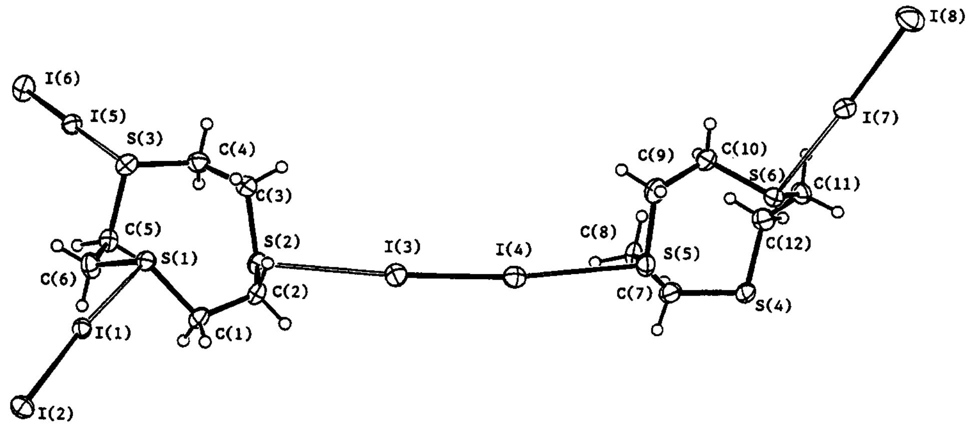

FIGURE 2 ORTEP view of 2[9]aneS$_3$ · 4I$_2$ (**I**). Thermal ellipsoids are drawn at the 30% probability level.

realized for the set of the prepared solutions and the sums of the squared deviations between the calculated and experimental absorbances. The closeness of the ϵ values, obtained at the five different temperatures, the low standard deviations of the *K*'s, and especially the correlation coefficient (r = 1.000) of the Arrhenius plot indicate the good reliability of the experimental data.

The ^{13}C NMR spectrum of [9]aneS$_3$ shows a unique peak at δ 34.74, which moves toward lower fields in the presence of increasing amounts of molecular diiodine [33]. The δ values as a function of the complex concentration, calculated using the spectrophotometric formation constant of the 1:1 complex, show deviations from linearity for [I$_2$]/[[9]aneS$_3$] molar ratios higher than 1:1 [34], thus indicating that the formation of 2:1 and 3:1 adducts cannot be neglected in the range of concentrations used for the NMR experiments. An attempt to measure the chemical shifts of each carbon atom for the 1:1 complex by lowering the temperature (down to −80°C) was unsuccessful in consequence of a decrease in complex solubility with diminishing temperature.

Three types of compounds have been isolated in the solid state with [9]aneS$_3$/I$_2$ ratios of 1:1, 1:2, and 1:3, respectively. The first compound has been obtained as a microcrystalline powder only, whereas the other two were obtained as crystals suitable for single-crystal structure determination. A perspective drawing of the 1:2 adduct (**I**) is reported in Figure 2.

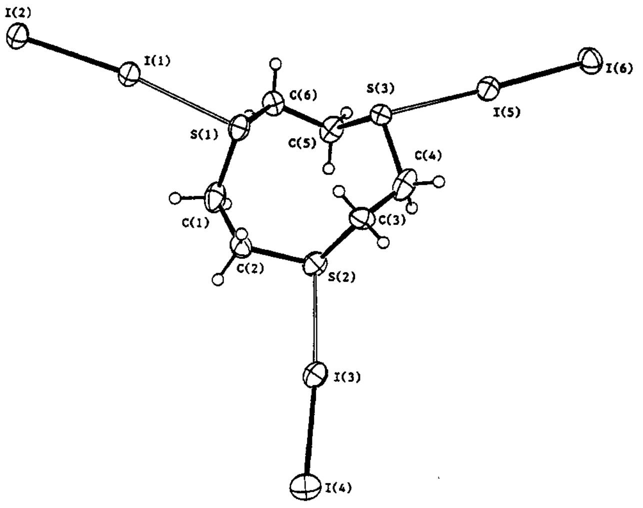

FIGURE 3 ORTEP view of [9]ane$S_3 \cdot 3I_2$ (**II**). Thermal ellipsoids are drawn at the 30% probability level.

On the basis of the S-I distances, the adduct can be envisioned as a weakly interacting diodine molecule (I(3)-I(4)), bridging two different units with composition [9]ane$S_3 \cdot 2I_2$ and [9]ane$S_3 \cdot I_2$, respectively. The bridging molecule has the shortest I-I distance (2.755(1) Å), to which long S-I distances (S(2)-I(3) 3.239(1) Å, S(5)-I(4) 3.089(1) Å) correspond. The other three I-I distances range between 2.781(1) and 2.818(1) Å, with corresponding S-I distances ranging between 2.887(1) and 2.792(1) Å.

The conformation of the two [9]aneS_3 rings is different, as can be seen in Table 5, where the torsional angles of the rings are reported. The C(7)-S(4) ring adopts a conformation with idealized C_3 symmetry in which the sp^3 hybridized S atoms are endodentate. This conformation is very close to the [333] one displayed in the solid state by [9]aneS_3 [35], which also corresponds to the lowest energy conformer of cyclononane. A less symmetric conformation is adopted instead by the C(1)-S(1) ring, and it does not correspond to one of the possible lowest energy minima for this ring. The latter kind of conformation is also found in the 1:3 adduct (**II**) shown in Figure 3, where all three sulfur atoms are binding I_2 molecules. The S···I and I-I distances are very similar to those found in **I** and other thioether compounds (Table 5).

In Table 6 are collected the geometrical parameters for the interaction of thioether sulfur atoms with the diiodine molecule for different adducts reported in the literature [36–39]. The S···I-I arrangement is essentially linear, and the values of *d*(S···I) and *d*(I-I) fall fairly close to the hyperbola reported in Ref. [9]. The S···I distances in the present compounds are definitely longer with respect to the interaction of thioketonic sulfur in several substrates [8,9], except for some thiohydantoins [11], in which similar distances have been found.

No particular feature is shown by the packing of the I_2 molecules; an inspection of the intermolecular I···I contacts of both **I** and **II** shows only a few interactions close to the sum of the van der Waals radii (ca. 4.0 Å), or slightly shorter.

For the three solid compounds, the FT-Raman bands due to *ν*(I-I) stretching vibrations dominate all the other bands attributable to the organic molecules and, as expected [12,20], are shifted to lower frequencies with respect to the value of 180 cm^{-1} found for solid I_2 [40]. Compound **I** shows two peaks at 159 and 171 cm^{-1}, which correspond to the two different types of diiodines; the peak at 171 cm^{-1}, with lower intensity, is attributable to the bridged I_2 (*d*(I-I) = 2.755 Å with respect to 2.715 Å, measured in pure I_2 [41]), while that at 159 cm^{-1}, with higher intensity and bandwidth, is attributable to the other three diiodine molecules with longer I-I distances (*d*(I-I) ranging between 2.781 and 2.818 Å). Compound **II** shows only one peak at 162 cm^{-1} with intensity and bandwidth similar to the band at 171 cm^{-1} of **I**, in accordance with the I-I bond lengths of the three coordinated diiodines (*d*(I-I) ranging between 2.751 and 2.772 Å). All these frequencies fit fairly well the linear correlation of *ν*(I-I) vs. *d*(I-I) obtained for weak or medium-weak complexes with I_2 [12,20]. The FT-Raman spectrum of the solid powder with [9]aneS_3/I_2 ratios of 1:1 shows one very strong and neat peak at 146 cm^{-1}, in accordance with the hypothesis of a 1:1 adduct. This frequency, which is lower than the values found in **I** and **II**, indicates that in the 1:1 adduct, the S···I_2 interaction is stronger than in the other two compounds [42] and, consequently, it induces a greater lengthening of the I–I bond, with a value of ≈2.83 Å, estimated on the basis of the linear *ν*(I-I)/*d*(I-I) correlation [12,20].

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[34] (a) For the equilibrium 1, the ^{13}C observed chemical shifts δ (ppm) are given by $\delta = \mathring{\delta}_D + (\mathring{\delta}_{DI_2} - \mathring{\delta}_D)[DI_2]/[D]^\circ$, where $[D]^\circ$ is the analytical concentration of the donor and $\mathring{\delta}_D$ and $\mathring{\delta}_{DI_2}$ the chemical shifts of the donor and the complex, respectively. (b) F. Cristiani, F. A. Devillanova, A. Diaz, F. Isaia, G. Verani, *Spectrosc. Lett., 25*, 1992, 865.

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