Reaction of Bis(morpholinothiocarbonyl) Disulphide with Iodine. Existence of a 1 : 1 Charge-Transfer Precursory Adduct in an Oxidation Reaction. Isolation and Crystal Structure of Bis[3,5-di(*N*-morpholinio)-1,2,4-trithiolane] Hexadecaiodide†

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The reaction of bis(morpholinothiocarbonyl) disulphide, $S_2[C(S)NC_4H_8O]_2$, with iodine in ratios ranging between 1 : 1 and 1 : 10 has been investigated in CH_2Cl_2 by spectrophotometric measurements. The immediate production of the known 1 : 1 charge-transfer complex between the reagents is observed. This species evolves according to a first-order rate law to give a brown compound which has been isolated from concentrated CH_2Cl_2 solutions of $I_2 + S_2[C(S)NC_4H_8O]_2$ mixtures. An *X*-ray crystal structure analysis of this compound indicated that the crystals are triclinic, space group $P\bar{1}$, with $a = 7.834(2)$, $b = 7.959(2)$, $c = 24.142(4)$ Å, $\alpha = 86.80(1)$, $\beta = 88.55(1)$, $\gamma = 70.86(1)°$, and $Z = 2$. The structure consists of bis[3,5-di(*N*-morpholinio)-1,2,4-trithiolane] cations, $[C_{10}H_{16}N_2O_2S_3]^{2+}$, and of discrete polyiodide anions $I_{16}{}^{4-}$.

The formation of molecular complexes between iodine and thiones has long been recognized.[1,2] In particular, extensive studies carried out on some tetra-alkylthiuram disulphides[2] have revealed that the carbonyl sulphur is the site of interaction with iodine at a 1:1 ratio, despite the several electron-donor sites available in the donor molecule. However, iodine also oxidizes thiuram disulphide co-ordinated to mercury, giving a dipositive five-membered ring.[3]

Since co-ordinative equilibria may be the initial steps in oxidative reactions, we are reinvestigating the reaction of iodine with dithio- and diseleno-carbamato-derivatives[4,5] in order to try and clarify the reaction mechanism. We have recently shown that the 1:1 charge-transfer (c.t.) adduct between iodine and bis(morpholinoselenocarbonyl) triselenide evolves to give an oxidation product identified as (*N*-morpholinecarbodiselenoato)selenium(II) iodide,[6] and in this paper we report a study on a similar reaction with bis(morpholinothiocarbonyl) disulphide.

Experimental

Materials.—Twice sublimed iodine was purchased from Carlo Erba. Dichloromethane was Merck Reagent Grade and dried over 4-Å molecular sieves before use. Bis(morpholinothiocarbonyl) disulphide, $S_2[C(S)NC_4H_8O]_2$, was prepared by oxidation of the inner salt, $[OC_4H_8NH_2]^+[OC_4H_8NCS_2]^-$, in aqueous solution with 6% hydrogen peroxide. The cream solid formed was filtered off, dried, and recrystallized twice from CH_2Cl_2–C_2H_5OH mixtures.

The compound $[OC_4H_8NCS_3CNC_4H_8O]_2{}^{4+}I_{16}{}^{4-}$, was obtained as red-brown lustrous crystals on prolonged standing of CH_2Cl_2 solutions of $S_2[C(S)NC_4H_8O]_2$ and iodine in a 1:4 ratio. The crystals are less soluble than the starting materials (Found: C, 9.35; H, 1.25; N, 2.30. Calc. for $C_{10}H_{16}I_8N_2O_2S_3$: C, 9.20; H, 1.25; N, 2.15%).

The elemental analyses were performed by the Istituto di Chimica Farmaceutica, Università di Cagliari. The u.v. spectrum is reported in Figure 1. I.r. (KBr pellet): 2 930mw, 2 900m, 2 830mw, 1 580mw, 1 562vw, 1 547mw, 1 535vw, 1 523vw, 1 445m, 1 433m, 1 410m, 1 396m, 1 380s, 1 303m, 1 265s, 1 218w, 1 182w, 1 106vs, 1 095vs, 1 055m, 1 037m, 1 025ms, 993w, 869m, 859m, 815w, 650w, 582m, 548m, 443m, and 410m cm^{-1}.

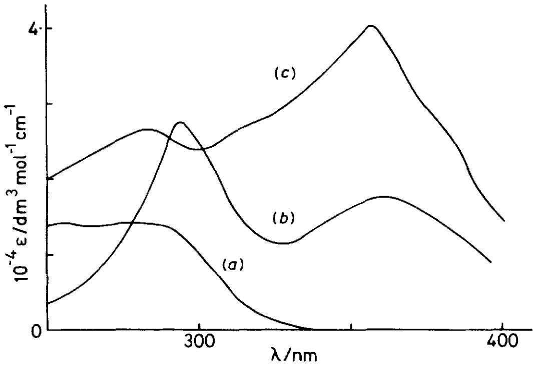

Figure 1. U.v. spectra in CH_2Cl_2 at 20 °C of (*a*) $S_2[C(S)NC_4H_8O]_2$, (*b*) $[C_{10}H_{16}N_2O_2S_3]_2I_{16}$, and (*c*) $S_2[C(S)NC_4H_8O]_2 \cdot I_2$

Spectroscopy.—U.v.-visible spectra were recorded on a Cary model 219 spectrophotometer equipped with a Lauda K2RD thermostat (±0.1 °C) using 1-cm and 0.1-cm matched quartz cells. Infrared spectra were recorded using a Perkin-Elmer model 983 spectrophotometer. Five dichloromethane solutions containing constant amounts of $S_2[C(S)NC_4H_8O]_2$ (1.02×10^{-3} mol dm^{-3}) and iodine in the 1:1, 1:2, 1:4, 1:8, and 1:10 ratios were monitored spectrophotometrically in the 250—500 nm region at 20 °C for some days.

Calculations.—The formation constant of the 1:1 complex formed immediately after mixing the reagents was calculated as previously described,[5] by using absorbance data at 26 regularly spaced wavelengths in the 250—500 nm range. If the molar absorptivities of each component of the reaction mixtures are

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† *Supplementary data available* (No. SUP 56205, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-*hydrogen* atoms

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
I(1)	−459(2)	4 314(2)	4 349(1)	N(1)	6 568(18)	854(17)	3 593(5)
I(2)	−12(2)	4 499(2)	3 184(1)	N(2)	8 720(18)	1 383(19)	1 605(6)
I(3)	911(2)	4 822(2)	1 970(1)	C(1)	6 604(22)	1 452(19)	3 096(8)
I(4)	2 753(2)	3 746(2)	662(1)	C(2)	7 998(25)	−719(24)	3 827(7)
I(5)	3 730(2)	2 752(2)	−400(1)	C(3)	8 392(27)	−347(27)	4 414(8)
I(6)	4 513(2)	1 253(2)	−1 686(1)	C(4)	5 567(30)	1 840(26)	4 545(8)
I(7)	5 703(2)	1 957(2)	−2 829(1)	C(5)	4 941(26)	1 713(29)	3 938(8)
I(8)	6 665(2)	2 778(2)	−3 938(1)	C(6)	7 798(22)	1 756(19)	2 058(8)
S(1)	8 488(6)	435(6)	2 663(2)	C(7)	10 465(25)	−50(26)	1 586(7)
S(2)	4 772(7)	3 079(7)	2 795(2)	C(8)	10 649(28)	−975(28)	1 060(7)
S(3)	5 934(7)	3 859(7)	2 074(2)	C(9)	8 573(25)	1 422(27)	590(8)
O(1)	6 779(20)	288(20)	4 746(5)	C(10)	8 172(26)	2 535(25)	1 079(7)
O(2)	10 394(19)	235(19)	591(5)				

known, the concentration of each species can be calculated by analysing the absorbances with a multiple linear regression program. In matrix notation, since $A = \varepsilon \cdot X$ where A is the $L \times 1$ matrix of experimental absorbances (L is the number of wavelengths), $\varepsilon = L \times M$ (M is the number of species in the reaction mixtures), and $X = M \times 1$, and since ε is known, X can be obtained as $X = (\varepsilon'\varepsilon)^{-1}\varepsilon' A$. Moreover, taking into account that the term $(\varepsilon'\varepsilon)^{-1} = E$ is the same for all examined solutions, we only have to calculate the matrix product $E \times A'$ to obtain the composition of each solution. These calculations were performed by means of a program written in BASIC for a HP-85 Hewlett-Packard personal computer.

X-Ray Crystal Structure Analysis.—*Crystal data.* $C_{10}H_{16}I_8N_2O_2S_3$, M = 1 307.665, triclinic, a = 7.834(2), b = 7.959(2), c = 24.142(4) Å, α = 86.80(1), β = 88.55(1), γ = 70.86(1)°, U = 1 419.8(6) Å^3, Z = 2, D_c = 3.059 g cm^{-3}, $F(000)$ = 1 156, Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 88.72 cm^{-1}, space group $P\bar{1}$.

The unit-cell parameters of a brownish red prismatic crystal of size 0.11 × 0.12 × 0.72 mm were refined by a least-squares procedure applied to the θ values of 23 reflections in the range 9—14° carefully measured on a Siemens AED single-crystal diffractometer.

Intensity data. Intensity data were collected at 295 K on the same diffractometer equipped with niobium-filtered Mo-K_α radiation and using the θ—2θ scan technique. All the reflections were measured, first with θ in the range 3—24° and then in the range 3—22°. The intensity of one standard reflection was checked every 50 reflections but no significant change in the measured intensities was observed during the data collection. Of a total of 3 383 independent reflections, 1 954 having $I \geqslant 2\sigma(I)$ were considered 'observed' and employed in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established first by Wilson's method[7] and then by least-squares refinement. Corrections for absorption (maximum and minimum values 1.309 78, 0.853 12) and extinction (maximum and minimum values 1.028 90, 0.919 94) were applied using the method of Walker and Stuart.[8]

Structure determination and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F using the SHELX system of computer programs,[9] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. All the H atoms were placed in their geometrically calculated positions and were refined by allowing them to ride on their bonded carbon atoms. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement and in the final cycles of refinement a weight $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was calculated where K = 0.3074 and g = 0.004 078. The final R value was 0.0384 for the observed reflections and R' was 0.0501 $\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. The final electron-density difference synthesis showed no peaks >0.74 and < −0.72 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 10. The final atomic co-ordinates are given in Table 1.

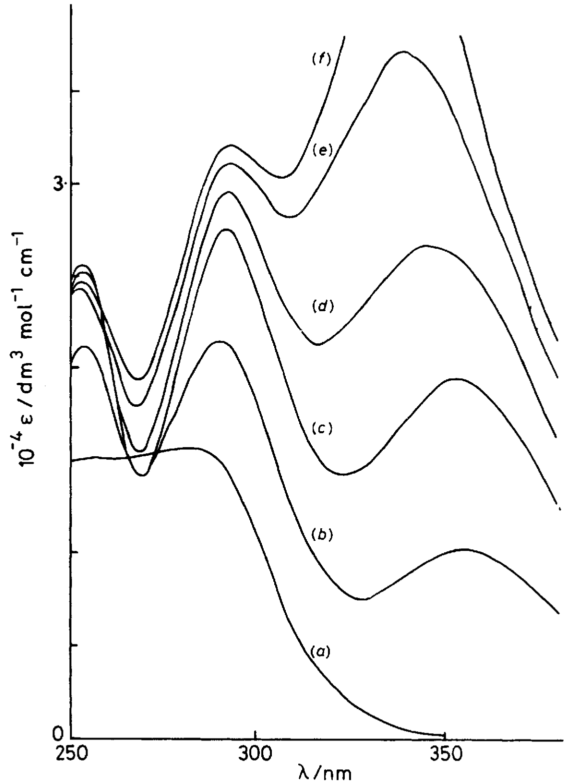


Figure 2. U.v. spectra in CH_2Cl_2 at infinite time of solutions having $[I_2]:[S_2\{C(S)NC_4H_8O\}_2]$ ratios of (*a*) 0:1, (*b*) 1:1, (*c*), 2:1, (*d*) 4:1, (*e*) 8:1, and (*f*) 10:1

The calculations were carried out on the CYBER 76 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (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 C.N.R. (Parma).' The programs ASSORB,[11] PARST,[12] PLUTO,[13] and ORTEP[14] were also used.

Results and Discussion

As is already known, the addition of iodine to $S_2[C(S)NC_4H_8O]_2$ in CH_2Cl_2 is accompanied by a change in the u.v.-visible spectrum of the solutions, indicating the formation of a c.t. complex (Figure 1). The formation constant at 20 °C for this 1:1 case was calculated as $K_{eq} = (1.2 \pm 0.1) \times 10^2$ dm^3 mol^{-1}, using the absorbance data obtained immediately after mixing the reagents.

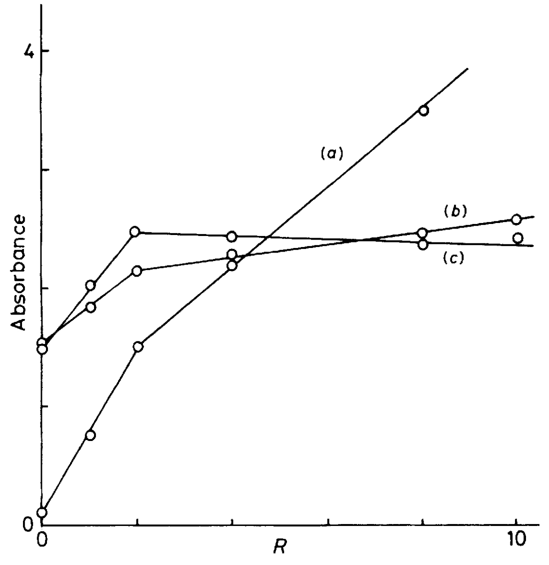


Figure 3. Plots of absorbance in CH_2Cl_2 at infinite time for at 330 (*a*), 280 (*b*), and 250 nm (*c*) *versus* the ratio (*R*) $[I_2]:[S_2\{C(S)NC_4H_8O\}_2]$

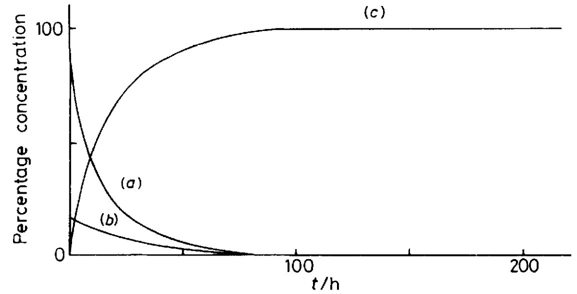


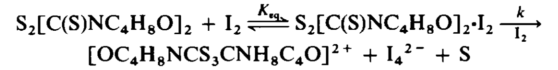
Figure 4. Relative concentration (%) *versus* time for (*a*) $S_2[C(S)NC_4H_8O]_2$, (*b*) $S_2[C(S)NC_4H_8O]_2{\cdot}I_2$, and (*c*) product P

By monitoring the absorbance with time, a slow evolution of the spectra is observed. Three new peaks at 253, 289, and 357 nm for solutions with ratios $[I_2]:S_2[C(S)NC_4H_8O]_2$ up to 1:2, and a further one at 337 nm for higher ratios, increase on standing (Figure 2). By plotting the absorbances at infinite time, at fixed wavelengths, *versus* the reagent ratio, curves such as those in Figure 3 are obtained. The linear part of the curves in Figure 3 is indicative of a reaction going to completion.

Knowing the concentrations of the different species at any time (Figure 4) as described in the Experimental section, it was possible to calculate $k_{obs.}$ from the second-order equation (1)

$$d[P]/dt = k_{obs.}([I_2] - [2P])([S_2\{C(S)NC_4H_8O\}_2] - [P]) \quad (1)$$

where P indicates the reaction product.* For all the analysed data a good linear behaviour ($r \geqslant 0.99$) is obtained. The mean $k_{obs.}$ is $(1.6 \pm 0.1) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The pathway Scheme 1

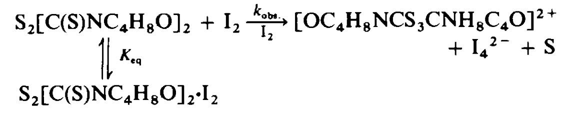


$$S_2[C(S)NC_4H_8O]_2 + I_2 \overset{K_{eq}}{\rightleftharpoons} S_2[C(S)NC_4H_8O]_2{\cdot}I_2 \xrightarrow[I_2]{k} [OC_4H_8NCS_3CNH_8C_4O]^{2+} + I_4^{2-} + S$$

Scheme 1.

may reasonably be suggested. The $k_{obs.}$ of equation (1) (second order with respect the starting reagents) is related to k through $k_{obs.} = K_{eq}k$ and therefore $k = (1.3 \pm 0.2) \times 10^{-5}$ s^{-1}. This kinetic constant (first order with respect to the c.t. complex) may be related to the transformation process of the c.t. complex to give the 3,5-di(*N*-morpholinio)-1,2,4-trithiolane cation.

The experimental data may be fitted to the alternative mechanism in Scheme 2. However Scheme 1 seems more



$$\begin{array}{l} S_2[C(S)NC_4H_8O]_2 + I_2 \xrightarrow[I_2]{k_{obs.}} [OC_4H_8NCS_3CNH_8C_4O]^{2+} + I_4^{2-} + S \\ \Big\Updownarrow K_{eq} \\ S_2[C(S)NC_4H_8O]_2{\cdot}I_2 \end{array}$$

Scheme 2.

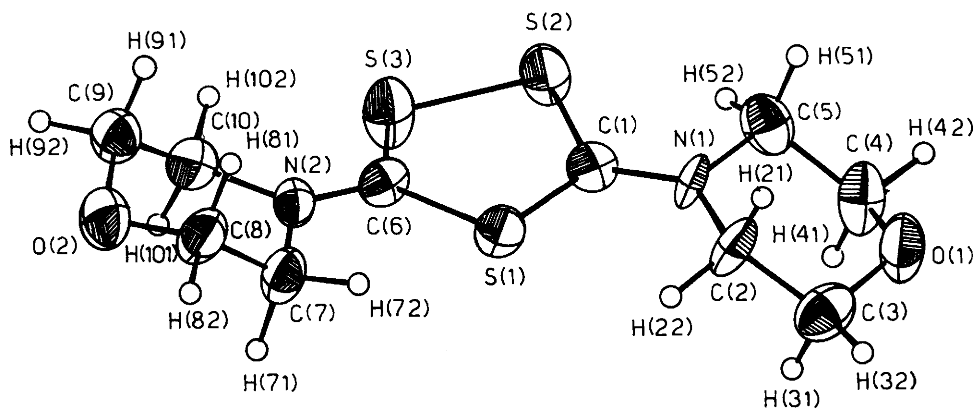


Figure 5. Perspective view of the cation. Thermal ellipsoids are drawn at the 40% probability level

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* The spectrum of P is very similar to that obtained by dissolving in CH_2Cl_2, in the same concentration range, the bis[3,5-di(*N*-morpholinio)-1,2,4-trithiolane] hexadecaiodide. It is very convenient that in this concentration range the ion I_{16}^{4-} dissociates to lower polyiodides, and that the additional strong peak at 337 nm, obtained for $[I_2]:[S_2\{C(S)NC_4H_8O\}_2]$ ratios higher than 2:1, is probably due to the formation of higher polyiodides.

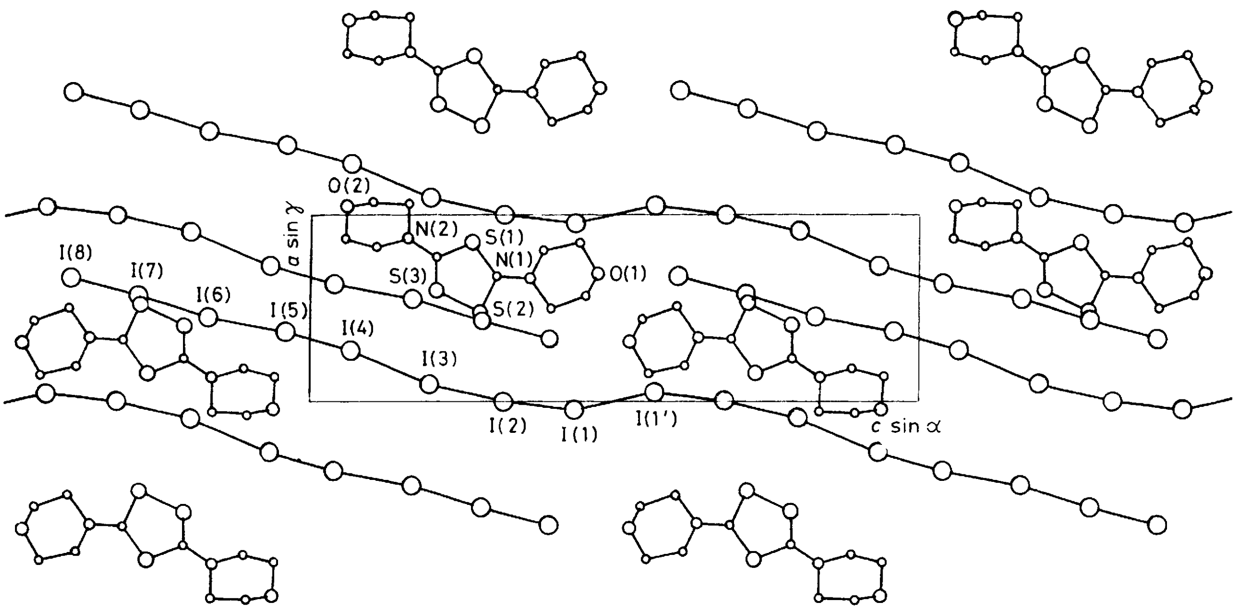

Figure 6. Projection of the structure viewed along *b*

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) In the anion

I(1)–I(1^{i})	3.550(3)	I(4)–I(5)	2.741(3)
I(1)–I(2)	2.827(3)	I(5)–I(6)	3.358(3)
I(2)–I(3)	3.018(3)	I(6)–I(7)	2.976(3)
I(3)–I(4)	3.471(3)	I(7)–I(8)	2.858(3)
I(2)–I(1)–I(1^{i})	147.2(1)	I(4)–I(5)–I(6)	172.3(1)
I(1)–I(2)–I(3)	172.4(1)	I(5)–I(6)–I(7)	144.9(1)
I(2)–I(3)–I(4)	161.4(1)	I(6)–I(7)–I(8)	177.2(1)
I(3)–I(4)–I(5)	170.9(1)		

(*b*) In the cation

N(1)–C(2)	1.47(2)	N(2)–C(7)	1.47(2)
C(2)–C(3)	1.52(3)	C(7)–C(8)	1.48(3)
C(3)–O(1)	1.44(2)	C(8)–O(2)	1.42(2)
O(1)–C(4)	1.39(2)	O(2)–C(9)	1.43(2)
C(4)–C(5)	1.58(3)	C(9)–C(10)	1.48(3)
C(5)–N(1)	1.49(2)	C(10)–N(2)	1.51(2)
N(1)–C(1)	1.27(2)	N(2)–C(6)	1.29(2)
C(1)–S(1)	1.78(2)	C(6)–S(1)	1.74(2)
C(1)–S(2)	1.73(2)	C(6)–S(3)	1.73(1)
S(2)–S(3)	2.04(1)		
N(1)–C(2)–C(3)	108.5(15)	N(2)–C(7)–C(8)	110.2(16)
C(2)–C(3)–O(1)	111.9(17)	C(7)–C(8)–O(2)	111.6(16)
C(3)–O(1)–C(4)	112.5(15)	C(8)–O(2)–C(9)	109.2(15)
O(1)–C(4)–C(5)	111.7(16)	O(2)–C(9)–C(10)	111.9(16)
C(4)–C(5)–N(1)	108.8(16)	C(9)–C(10)–N(2)	110.3(15)
C(5)–N(1)–C(2)	119.1(13)	C(10)–N(2)–C(7)	115.9(14)
C(1)–N(1)–C(2)	122.8(14)	C(6)–N(2)–C(7)	122.1(15)
C(1)–N(1)–C(5)	117.9(14)	C(6)–N(2)–C(10)	121.6(15)
N(1)–C(1)–S(1)	119.6(12)	N(2)–C(6)–S(1)	120.7(13)
N(1)–C(1)–S(2)	122.3(13)	N(2)–C(6)–S(3)	119.6(12)
C(1)–S(1)–C(6)	99.2(8)	S(3)–S(2)–C(1)	100.2(7)
S(1)–C(6)–S(3)	119.6(11)	S(2)–C(1)–S(1)	117.7(11)
C(6)–S(3)–S(2)	98.9(6)		

Symmetry operation: i $\bar{x},\bar{y},\bar{z}$

Table 3. Conformational analysis of the cation

(*a*) Torsion angles (°)

C(5)–N(1)–C(2)–C(3)	−46(2)	C(10)–N(2)–C(7)–C(8)	−44(2)
N(1)–C(2)–C(3)–O(1)	52(2)	N(2)–C(7)–C(8)–O(2)	55(2)
C(4)–O(1)–C(3)–C(2)	−64(2)	C(9)–O(2)–C(8)–C(7)	−65(2)
C(3)–O(1)–C(4)–C(5)	60(2)	C(8)–O(2)–C(9)–C(10)	63(2)
O(1)–C(4)–C(5)–N(1)	−48(2)	O(2)–C(9)–C(10)–N(2)	−51(2)
C(2)–N(1)–C(5)–C(4)	43(2)	C(7)–N(2)–C(10)–C(9)	43(2)
C(2)–N(1)–C(1)–S(1)	−3(2)	C(7)–N(2)–C(6)–S(1)	−6(2)
C(5)–N(1)–C(1)–S(2)	−6(2)	C(10)–N(2)–C(6)–S(3)	−2(2)
C(6)–S(1)–C(1)–N(1)	180(1)	C(1)–S(1)–C(6)–N(2)	−174(1)
S(3)–S(2)–C(1)–N(1)	171(1)	S(2)–S(3)–C(6)–N(2)	165(1)
C(6)–S(1)–C(1)–S(2)	6(1)	C(1)–S(1)–C(6)–S(3)	10(1)
S(3)–S(2)–C(1)–S(1)	−17(1)	S(2)–S(3)–C(6)–S(1)	−19(1)
C(1)–S(2)–S(3)–C(6)	19(1)		

(*b*) Asymmetry parameters (°)

ΔC_s[C(2)]	11	ΔC_s[C(8)]	13
ΔC_s[O(1)]	4	ΔC_s[O(2)]	3
ΔC_s[C(2)]	14	ΔC_s[C(7)]	16
ΔC_2[C(2)–C(3)]	18	ΔC_2[C(7)–C(8)]	21
ΔC_2[N(1)–C(2)]	13	ΔC_2[N(2)–C(7)]	13
ΔC_2[N(1)–C(5)]	6	ΔC_2[N(2)–C(10)]	8
ΔC_2[S(1)]	3		

appropriate on the grounds: (*i*) $k_{\text{obs.}}$ seems to be related to a slower process than in a simple oxidative process; (*ii*) a comparison with the similar reactions of the selenium analogues[6] shows that the obtained constant *k* is very similar to that for the evolution process of the c.t. complex; (*iii*) it is generally found that the time dependence of the c.t. band is due to the transformation of an initially formed 1:1 outer-sphere complex into the inner-sphere complex, followed by rearrangement.[15]

We conclude that the c.t. adduct formed between iodine and $S_2[C(S)NC_4H_8O]_2$ undergoes oxidation and rearrangement to give the stable cation probably *via* the inner-sphere complex.

On the basis of our results the presence of HgI_2, to achieve the oxidation of tetra-alkylthiuram disulphides by iodine, is seen to be unnecessary, as proposed earlier.[3] The presence of a suitable counter ion probably provides a favourable environment to stabilize the cation.

Crystal Structure.—The structure consists of 3,5-di(*N*-morpholinio)-1,2,4-trithiolane cations, $[C_{10}H_{16}N_2O_2S_3]^{2+}$, and of discrete polyiodide anions I_{16}^{4-}. The nature of the bonding to the trithiolane ring is $>\overset{+}{N}=C<$. Figure 5 shows the geometry and the atom-numbering scheme of the organic cation, and Table 2 lists distances and angles involving all the non-hydrogen atoms.

In the organic cation the five-membered ring adopts a twisted conformation and both morpholinium rings show the usual distorted-chair conformation as indicated by the torsion angles and by the asymmetry parameters[16] reported in Table 3. The theoretical χ^2 values at 95% for nine degrees of freedom indicate that the two halves of the cation are not significantly different and a pseudo-two-fold axis passes through S(1) and the midpoint of S(2)–S(3). Beurskens *et al.*[17] previously reported the structure of the 3,5-bis(*N*,*N*-diethyliminio)-1,2,4-trithiolane cation in its $[Hg_2I_6]^{2-}$ salt which contains the same penta-atomic ring. A similar penta-atomic ring conformation constrained by crystal symmetry is also observed in the diphenylhydrazone of 1,2,4-trithiolane-3,5-dione,[18] and in 3,5-bis(isopropylidene)-1,2,4-trithiolane[19] where the sulphur atoms lies on a crystallographic two-fold axis. The bond distances and values in the trithiolane ring are in agreement with those observed in the above compounds, in 3,5-bis(2′-oxocyclopentyl)-1,2,4-trithiolane,[20] and in 3,5-bis(pivaloylmethylene)-1,2,4-trithiolane,[21] and indicate a π resonance delocalization. The bond lengths and angles in the two morpholinium moieties are not significantly different.

The counter ion of this large organic cation is an unusual polyiodide ion which occurs as discrete I_{16}^{4-} units. There have been few *X*-ray crystal structure characterizations for the higher polyiodides I_7^-, I_8^{2-}, I_9^-, and I_{16}^{4-}; these have revealed that although they have many geometrical features in common, the ions differ in detail. The I_{16}^{4-} ion consists of a sequence of I_3^- and I_2 units of the type $I_3^- \cdots I_2 \cdots I_3^-$. $I_3^- \cdots I_2 \cdots I_3^-$ in which two centrosymmetric I_8^{2-} units exhibit a non-negligible interaction [3.550(3) Å]. As observed for other I_8^{2-} moieties, two asymmetric and bent I_3^- units are weakly bonded to an I_2, which exhibits an elongated I–I bond [2.741(3) Å] compared to solid I_2 (2.68 Å),[22] but which is one of the smallest observed: 2.748(2),[23] 2.753(1),[24] 2.76,[25] 2.773,[26] 2.78 and 2.791,[27] 2.797(3) and 2.805(5),[28] and 2.83 Å.[29] The more symmetric I(6)–I(7)–I(8) with I–I bonds of 2.976(3) and 2.858(3) Å is linked to I(5) by an interaction [3.358(3) Å] stronger than that between the more asymmetric I(1)–I(2)–I(3) [I–I 2.827(3) and 3.018(3) Å] with I(4) [3.471(3) Å]. An apposite pattern linkage is observed in the complexes [ML]-$[I_8]$[28] (M = Pd^{II} or Pt^{II}, L = tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]-tetra-azacyclohexadecine) where the $I_3^- \cdots I_2$ interactions are weaker. In the I_{16}^{4-}, each centrosymmetric I_8^{2-} moiety, roughly planar [maximum deviation: 0.268(2) Å for I(3)], reveals an outstretched Z shape as observed in $[(CH_2)_6N_4CH_3]_2I_8$,[26] while in 3,7-dimethylxanthine–octaiodomercurate (2/1),[25] the I_{16}^{4-} anion assumes an S shape. The structure (Figure 6) consists of chairs of polyiodide anions interposed by organic cations held together by interactions of the type I $\cdots$ S, the most relevant of which are: I(3) $\cdots$ S(2) 3.505(5), I(2) $\cdots$ S(2) 3.656(6), I(3) $\cdots$ S(3) 3.747(6), I(7) $\cdots$ S(3) $(1 - x, 1 - y, -z)$ 3.835(6), and I(7) $\cdots$ S(2) $(1 - x, 1 - y, -z)$ 3.836(6) Å.

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