

removed in vacuo to yield crude **11b** (547 mg): IR 3450 (br), 2990 (s), 2885 (m), 2840 (w), 1800 (w), 1475 (m), 1378 (m), 1358 (m), 1066 cm^{-1} (s). Thermolysis of **11b** following the method described above for **11a** also gave **5** (62 mg, 15%).

Photolysis of 4,4-Dimethyl-1-(trimethylsilyl)-1-pentyn-3-one (7) and 2,3-Dimethyl-2-butene (2). A solution of **7**⁴ (456 mg, 2.5 mmol) and **2** (1.052 g, 12.5 mmol) in C_6H_6 (50 mL) was irradiated in the usual fashion. After 6 h, VPC analysis (column, C, 115 °C) indicated ~10% of **7** remaining and the formation of two products. Removal of solvent and bulb-to-bulb distillation of this residue (80–130 °C, 0.1 torr) yielded an oil (525 mg, 80%) that was subjected to preparative VPC. First eluted was **6b** (12%): IR 3055 (w), 2975 (s), 2165 (w), 1477 (m), 1384 (m), 1360 (m), 1244 (s), 1069 (s), 832 cm^{-1} (s); NMR (60 MHz) δ 1.43, 1.31, 1.25, 1.17, 1.07 (all s, total 21 H), 0.19 (s, 9 H). Anal. ($\text{C}_{16}\text{H}_{30}\text{OSi}$) C, H. The second component (68%) was **8**: IR 3100 (w), 2975 (s), 1679 (w), 1652 (w), 1384 (w), 1374 (w), 1362 (m), 1241 (s), 1189 (s), 941 (m), 880 (m), 840 cm^{-1} (s); NMR (60 MHz) δ 4.73 (m, 2 H), 2.68 (br s, 2 H), 1.72 (m, 3 H), 1.31 (s, 2 H), 1.20 (s, 3 H), 0.88 (s, 3 H), 0.06 (s, 9 H). Anal. ($\text{C}_{16}\text{H}_{30}\text{OSi}$) C, H.

Flash chromatography³⁹ using 1.5% Et_2O /hexanes of the oil (277 mg) obtained from the photolysate gave **25** (141 mg, 51%): IR 3075 (w), 2985 (s), 2875 (m), 1622 (m), 1385 (m), 1370 (m), 1363 (m), 1245 (s),

1147 (m), 969 (m), 871 (m), 847 (s), 780 cm^{-1} (w); NMR (300 MHz) δ 4.68 (s, 1 H), 1.15, 1.13, 1.12, 1.10, 1.03, 0.94 (all s, 18 H), 0.735 (d, $J = 6.0$ Hz, 1 H), 0.707 (d, $J = 6$ Hz, 1 H), 0.175 (s, 9 H); mass spectrum m/z 266.2070 (M^+ , calcd for $\text{C}_{16}\text{H}_{30}\text{SiO}$, 266.2074).

Thermolysis of (E)-1,1,5,5,6,6-Hexamethyl-7-((trimethylsilyl)methylene)-4-oxaspiro[2.4]heptane (25). Solutions of **25** in C_6D_6 in sealed tubes were heated and monitored by NMR spectroscopy. At 100 °C, **25** quantitatively rearranged to **8** within 0.5 h; at 75.0 °C, 47% of **25** had rearranged in 0.75 h.

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Registry No. **2**, 563-79-1; **4**, 62688-81-7; **5**, 88036-37-7; **6a**, 88036-38-8; **6b**, 88036-39-9; **7**, 53723-94-7; **8**, 88036-40-2; **11a**, 88036-41-3; **11b**, 88036-42-4; **19**, 88036-43-5; **22**, 88036-44-6; **23**, 88036-45-7; **25**, 88056-70-6.

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Interaction of Thiones with Molecular Diiodine.¹ The Crystal Structures of Dithizone–Diiodine, Ethylenethiourea–Bis(diiodine), Bis(ethylenethiourea)–Tris(diiodine), Bis(dithizone)–Heptakis(diiodine), and 1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium Triiodide–(Ethylenethiourea–Diiodine)

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Abstract: The crystal structures of four neutral charge-transfer molecular compounds formed between dithizone or ethylenethiourea, as donors, and diiodine, as acceptor, are described. Dithizone– I_2 is monoclinic ($a = 12.233$ (8) Å, $b = 11.713$ (8) Å, $c = 12.030$ (8) Å, $\beta = 102.8$ (1)°, $Z = 4$, space group $P2_1/n$; $R_F = 0.059$) and contains discrete moieties of the molecular formula with the diiodine fragment approximately normal to the dithizone fragment. Ethylenethiourea– $2(\text{I}_2)$ is triclinic ($a = 10.276$ (7) Å, $b = 9.176$ (6) Å, $c = 6.792$ (5) Å, $\alpha = 105.1$ (1)°, $\beta = 81.0$ (1)°, $\gamma = 96.4$ (1)°, $Z = 2$, space group $P\bar{1}$; $R_F = 0.041$) and contains discrete moieties of the molecular formula; the moiety as a whole has the shape of a twisted U. 2(Ethylenethiourea)– $3(\text{I}_2)$ is triclinic ($a = 9.362$ (6) Å, $b = 9.176$ (6) Å, $c = 7.434$ (5) Å, $\alpha = 116.9$ (1)°, $\beta = 72.5$ (1)°, $\gamma = 114.7$ (1)°, $Z = 1$, space group $P\bar{1}$; $R_F = 0.063$) and has a centrosymmetric twisted-chain structure with three iodine molecules held between the two donor molecules; this structure is similar to that of bis(((triphenylphosphine sulfide-*S*)iodine)-*I*)iodine (Bransford; Meyers *Cryst. Struct. Commun.* **1978**, *7*, 697–702). 2(Dithizone)– $7(\text{I}_2)$ is triclinic ($a = 13.312$ (8) Å, $b = 20.637$ (7) Å, $c = 9.746$ (6) Å, $\alpha = 101.8$ (1)°, $\beta = 87.1$ (1)°, $\gamma = 109.4$ (1)°, $Z = 1$, space group $P\bar{1}$; $R_F = 0.086$) and has a centrosymmetric, branched twisted chain of iodine molecules held at its ends by strong sulfur–iodine interactions. Intermediate between these neutral structures and the polyiodide salts is the salt–molecule complex 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide–(ethylenethiourea–diiodine) (monoclinic, $a = 11.102$ (7) Å, $b = 11.193$ (7) Å, $c = 9.551$ (6) Å, $\beta = 110.0$ (1)°, $Z = 2$, space group $P2_1$; $R_F = 0.051$), which contains discrete moieties of ethylenethiourea– I_2 together with the cations and anions of the second component. For these compounds, and some others, the values of $d(\text{S}-\text{I})$ plotted against $d(\text{I}-\text{I})$ fall on an approximately hyperbolic curve.

Diiodine (I_2) forms 1:1 molecular compounds of the charge-transfer type with a variety of molecules containing oxygen, nitrogen, sulfur, or selenium heteroatoms. Many crystal structures have been reported.^{3,4} Diiodine in combination with ionic iodide

species (as I^- or I_3^-) forms a large range of oligomeric anionic polyiodides; again many crystal structures have been reported.^{5,6}

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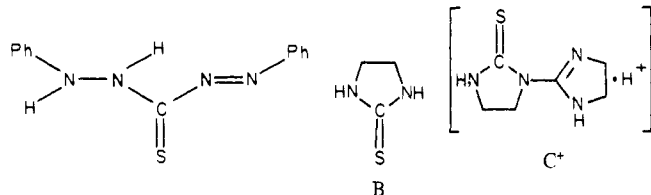
Table I. Crystal Data

	dithizone-I ₂	ethylene-thiourea-2(I ₂) ^c	2(ethylene-thiourea)-3(I ₂) ^d	2(dithizone)-7(I ₂) ^e	[C ⁺ I ₃ ⁻]-[B·I ₂] ^f
F wt	509.8	589.6	925.4	2289.3	902.88
F(000)	960	532	426	1010	810
a, Å	12.233 (8)	10.276 (7)	9.362 (6)	13.312 (8)	11.102 (7)
b, Å	11.713 (8)	9.970 (6)	9.176 (6)	10.637 (7)	11.193 (7)
c, Å	12.030 (8)	6.792 (5)	7.434 (5)	9.746 (6)	9.551 (6)
α, deg		105.1 (1)	116.9 (1)	101.8 (1)	
β, deg	102.8 (1)	81.0 (1)	72.5 (1)	87.1 (1)	110.0 (1)
γ, deg		96.4 (1)	114.7 (1)	109.4 (1)	
V, Å ³	1681.0	661.7	512.5	1273.9	1115.3
D _{meas} , g cm ⁻³	2.01 ^a			2.85 ^b	
D _{calcd} , g cm ⁻³	2.01	2.959	2.988	2.984	2.689
Z	4	2	1	1	2
space group	P2 ₁ /n	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P2 ₁
μ(Mo Kα), cm ⁻¹	36.0	97.0	87.0	87.1	67.0

^a The liquid used for the density measurement was a mixture of 1,1,2,2-tetrabromoethane and toluene. I suggest *p*-(tetrabromoethane)-toluene. ^b Nessler's reagent, partial decomposition. ^c The unit cell given for ethylenethiourea-2(I₂) is the Dirichlet reduced cell³⁴ in direct space but with the origin shifted from the conventional, triacute cornered origin. ^d The unit cell given for 2(ethylenethiourea)-3(I₂) is not a reduced cell. The reduced cell (in both Dirichlet and Delaunay senses) has *a* = 8.817 Å, *b* = 9.362 Å, *c* = 7.434 Å, α = 107.5°, β = 111.9°, γ = 100.4°. ^e The unit cell given for 2(dithizone)-7(I₂) is the Dirichlet reduced cell in direct space but with the origin shifted. ^f 1-(1-Imidazolin-2-yl)-2-thioxoimidinium triiodide-(ethylenethiourea-diiodine).

Although fewer oligomeric polyiodide cations are known, their number is increasing.⁷ However, only one neutral moiety containing more than a single diiodine molecule (bis(((triphenylphosphine sulfide-S)iodine)-I)iodine) appears to have been described.⁸

We have now found that the family of neutral molecular compounds, with S as heteroatom in the donor and poly(diiodine) moieties as acceptors, is an extensive one, and we present crystal structure analyses of compounds with formulas A·I₂, B·(I₂)₂, B₂·(I₂)₃, and A₂·(I₂)₇, where A = dithizone (1,5-diphenylthiocarbazono) and B = ethylenethiourea (2-imidazolidinethione).

tautomeric structures for A, B, and C⁺ are possible

The present and earlier structural results suggest that two series of compounds are involved. In the first of these, diiodine chains of varying lengths are attached to sulfur—the examples considered here are A·I₂ and B·(I₂)₂. The second series can be considered to start with 2(merocyanine)-I₂,⁹ where I₂ bridges between two thione sulfurs, and to proceed through B₂·(I₂)₃ (and its triphenylphosphine sulfide analogue⁸) to the branched (I)·I₅·I₂·I₃·(I) chain found in A₂·(I₂)₇.¹⁰

Table II. Comparison of Dimensions in 2(Ethylenethiourea)-3(I₂) and 2(Triphenylphosphine Sulfide)-3(I₂)

The image shows the chemical structure of the complex x = (Ph₃P)₂S(I-I)₂S(Ph₃P)₂. It consists of two triphenylphosphine sulfide (Ph₃P=S) groups coordinated to a central diiodine chain (I-I) through their sulfur atoms. The structure is shown as a chain of atoms: x-S, I₁-I₂---I₃, and another S atom coordinated to a Ph₃P group.

	2(ethylene-thiourea)-3(I ₂)	2(triphenylphosphine sulfide)-3(I ₂)
Distances		
S-I(1)	2.580 (7)	2.729 (2)
I(1)-I(2) ^a	2.948 (3)	2.838 (1)
I(2)-I(3)	3.472 (3)	3.570 (1)
I(3)-I(3') ^a	2.760 (5)	2.757 (2)
Angles		
C(P)-S-I(1)	102.8 (9)	107.0 (1)
S-I(1)-I(2)	85.1 (1)	96.30 (4)
I(2)-I(3)-I(3')	177.5 (2)	176.67 (5)

^a These values are for formal I₂ molecules and should be compared with *d*(I-I) in gaseous I₂ (2.667 (2) Å is the unweighted mean of the available values¹⁶) and in crystalline I₂ at 110 K (2.715 (6) Å¹⁷).

In addition we have determined the structure of a salt-molecule complex in which the components are the salt 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide (= C⁺I₃⁻) and the molecular compound ethylenethiourea-I₂. The weak interactions between I₂ and I₃⁻ suggest that this complex may represent an intermediate stage between neutral molecular compounds and polyiodide salts.

Experimental Section

Compound Preparation. Dithizone-I₂ was prepared by following Irving and Ramakrishna.¹¹

Ethylenethiourea was prepared by standard procedures from 1,2-diaminoethane and CS₂.¹² The compound B·(I₂)₂ was prepared by dissolving ethylenethiourea in dichloromethane and then adding a saturated solution of I₂ in dichloromethane. The compound B₂·(I₂)₃ was obtained by dissolving ethylenethiourea in water and adding an ethanolic solution of I₂. An identical product formed when ethylenethiourea was refluxed in ethanol previously saturated with I₂. 2(Dithizone)-7(I₂) was obtained by mixing 100 mg of dithizone (0.4 mmol) in 10 mL of CHCl₃ with 400 mg of I₂ (1.6 mmol) in 20 mL of CHCl₃, boiling under reflux for 30 min, and allowing the solution to crystallize overnight.

Following Johnson and Edens,¹³ we reacted ethylenethiourea in water with aqueous KI + I₂ solution and obtained, after recrystallization from

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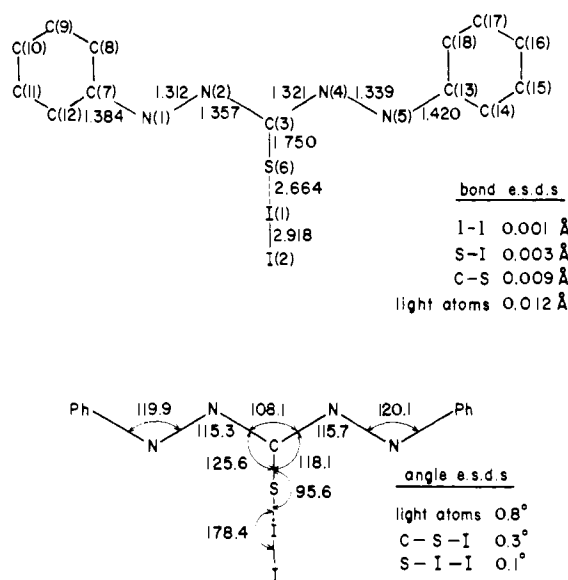
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Table III. Geometrical Parameters for Interaction of Thione Group with the Diiodine Molecule^a

moiety	$X_2C=S---I(1)-I(2)$					ref												
	$d[S-I(1)]$, Å	$d[I(1)-I(2)]$, Å	$\angle S-I(1)-I(2)$, deg	$\angle C=S-I(1)$, deg	torsion angle $X-C=S-I(1)$, deg													
ethylenethiourea-2(I ₂)	2.487 (3)	3.147 (1)	177.9 (1)	102.4 (2)	4.2 (1.4)	<i>b</i>												
2(dithizone)-7(I ₂)	2.506 (8)	3.215 (3)	179.1 (2)	100.4 (5)	83.4 (1.7)	<i>b</i>												
2(ethylenethiourea)-3(I ₂)	2.580 (7)	2.984 (3)	177.5 (2)	102.8 (9)	3.7 (2.6)	<i>b</i>												
ethylenethiourea-I ₂ in (C ⁺ I ₃ ⁻)·A·I ₂	2.588 (8)	2.987 (2)	178.2 (2)	101.2 (4)	6.8 (2.5)	<i>b</i>												
dithizone-I ₂	2.664 (3)	2.918 (1)	178.4 (1)	95.6 (3)	78.5 (6)	<i>b</i>												
N-methylthiocaprolactam-I ₂	2.688 (2)	2.888 (1)	176.21 (4)	109.9 (2)	4.4 (6)	21												
2(triphenylphosphine sulfide)-3(I ₂)	2.729 (2)	2.838 (1)	175.23 (5)	P-S-I(1)		Et												
				S-I(2)														
{	benzyl sulfide-I ₂	2.78 (2)	2.819 (9)	178.9	92.8	22a												
							Co(C ₅ H ₅ N) ₄ (NCS) ₂ -2(I ₂)	2.797 (2)	2.804 (1)	178.8 (1)	95.2 (3)	22b						
													1,4-dithiane-2(I ₂)	2.867 (6)	2.787 (2)	177.9 (4)	101.9 (1)	4

^a Some other sulfur-iodine interactions are included for comparison and are enclosed in a brace. I(1) in this table is the iodine linked to sulfur; atom numbering used in references has been altered where necessary. The sum of single bond covalent radii for S and I is 2.37 Å (Wells³⁵). The bond distance between I and three-coordinate S in S₂I⁺ is 2.342 (3) Å, and this bond has been assigned a bond order of 1.³⁶ The sulfur-iodine bond has been extensively reviewed.³⁷ For some I-I distances see Table II. ^b Present investigation.

Figure 1. Dithizone-I₂, molecular dimensions and numbering of atoms.

ethanol-water, red crystals of [C⁺I₃⁻]·[B·I₂]. This reaction is discussed later.

All the crystals were deeply colored.

Crystal Measurements. After preliminary diffraction photography to check crystal quality and determine unit cell symmetry and approximate dimensions, suitable crystals were sealed into thin-walled glass capillaries and mounted on a Philips PW-1100 four-circle diffractometer. Crystal data are given in Table I. Elemental analyses were not made as the compositions of the crystals emerged from the crystal data and were substantiated by the structure analyses. Details of the intensity measurements are given in Table II. Graphite-monochromated Mo K α ($\lambda = 0.71069$ Å) was used for all diffractometer measurements.

Solution and Refinement of Structures. The crystal structures were generally solved by a combination of Patterson and direct (MULTAN¹⁴) methods and refined by standard least-squares techniques. The SHELX-76

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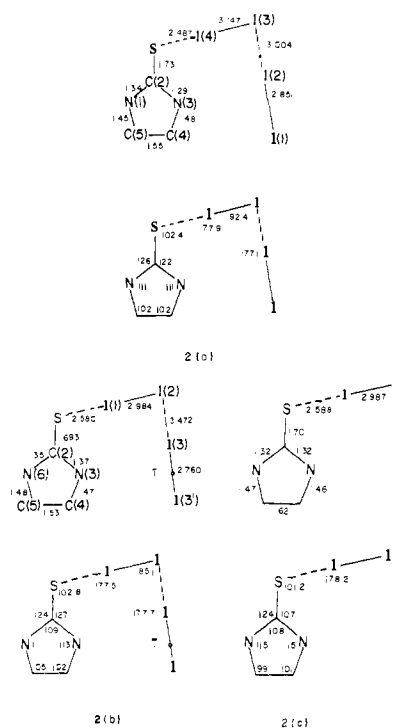


Figure 2. Bond lengths and angles in moieties involving ethylenethiourea and iodine: (a) ethylenethiourea-2(I₂), (b) 2(ethylenethiourea)-3(I₂), (c) ethylenethiourea-I₂ in the salt-molecule complex (C⁺I₃⁻)(A·I₂). In these and other analogous diagrams, the formally secondary interactions have been inserted as dashed lines, whereas the actual bonding pattern should be inferred from the dimensions of the moiety. Esds in (a): $\sigma(I-I) \sim 0.001$, $\sigma(I-S) \sim 0.003$, $\sigma(S-C) \sim 0.01$, $\sigma(C-C) \sim 0.01-0.02$ Å; $\sigma(I-I-I) \sim 0.04^\circ$, $\sigma(I-I-S) \sim 0.1^\circ$, $\sigma(C-N-C) \sim 1^\circ$. For (b) and (c) the esds are 2-3 times as large.

program set was used throughout. Hydrogen atoms were not located in any of the structure analyses. Details have been deposited. Cell data and R_F values are in the Abstract.

Results

Dithizone-I₂. The dithizone-I₂ moieties form discrete units in the crystal and the closest contacts between different moieties correspond to van der Waals interactions. The dithizone fragment is in a planar anti, s-trans conformation (Figure 1); the C, N, and S atoms extend from the mean dithizone plane by less than 0.08 Å. The linear S---I-I fragment is arranged almost orthogonally to this plane, with $\angle C-S-I = 95.6$ (3)°. A plane defined by C(3), S(6), I(1), and I(2) intersects the plane of the dithizone part at an angle of 101.6°. Thus the dithizone-I₂ moiety has roughly

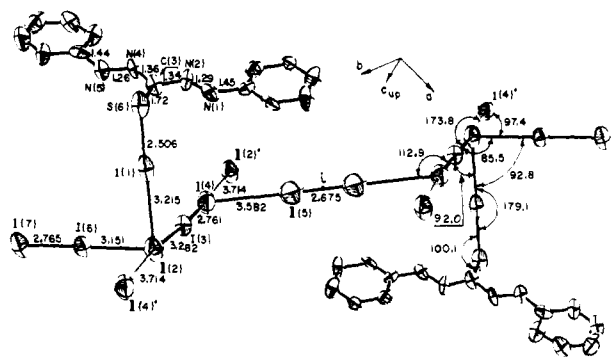


Figure 3. 2(Dithizone)-7(I₂)—dimensions of the centrosymmetric formula unit. The ellipsoids are 50% probability distributions.

the shape of a garden rake, where the S---I fragment is the handle of the rake and the dithizone fragment constitutes the toothed part.

Ethylenethiourea-2(I₂). The ethylenethiourea (I₂)₂ moieties form discrete units in the crystal, and the closest contacts between different moieties correspond to van der Waals interactions. The ethylenethiourea-2(I₂) moiety has the four iodine atoms and the sulfur in one plane, while the ethylenethiourea fragment is also essentially planar (Figure 2a); however, these two planes are mutually perpendicular with the N-C-S-I torsion angle close to 0° (see Table III).

2(Ethylenethiourea)-3(I₂). The 2(ethylenethiourea)-3(I₂) moieties form discrete units in the crystal, and the closest contacts between different moieties correspond to van der Waals interactions. The B₂(I₂)₃ moiety is centrosymmetric, with its center at a crystallographic symmetry center (Figure 2b). The atoms S, I(1), I(2), I(3), and their centrosymmetrically related partners are approximately coplanar, while the ethylenethiourea groups protrude approximately normal to the sulfur-iodine plane. The torsion angle N-C-S-I is close to 0° (Table III). The moieties 2(ethylenethiourea)-3(I₂) and 2(triphenylphosphine sulfide)-3(I₂) have closely similar overall shapes, and this is supported by the general similarity in bond and torsion angles. However, the interatomic distances (Table II) show that there are differences in the strengths of the S-I interactions in the two moieties, and this invokes other differences. In 2(triphenylphosphine sulfide)-3(I₂) the S---I interaction is weaker than in 2(ethylenethiourea)-3(I₂), with the consequence that bonding in the adjacent iodine molecule is less affected. The bridging I₂ molecules are somewhat extended with respect to the I-I distance in crystalline I₂,¹⁷ a similar effect is found in many polyiodides.^{18,19} From these comparisons one may conclude that ethylenethiourea is a considerably stronger donor to I₂ than is triphenylphosphine sulfide.

2(Dithizone)-7(I₂).¹⁰ In contrast to the three structures described above, there is one set of intermoleity I---I distances that is appreciably shorter than the van der Waals distance; $d(I(2)---I(4')) = 3.714 \text{ \AA}$, compared to a van der Waals distance of 4.2–4.3 Å. Although this means that any discussion of the 2-(dithizone)-7(I₂) moiety as an isolated entity can be only a first approximation, it is convenient to start the description of the structure (Figure 3) with such an approach, ignoring also (for the moment) any grouping of the iodine atoms into molecules. The iodine atoms I(7), I(6), I(2), I(3), I(4), I(5), and their centrosymmetrically related partners form an approximately planar array, lying in the (110) planes. A dithizone-I₂ fragment, with a shape very similar to that of the analogous molecule in crystalline dithizone-I₂ (i.e., the torsion angle N-C-S-I is close to 90°), is attached at I(2), with the I(2)-I(1)---S line approximately perpendicular to the plane of the iodines.

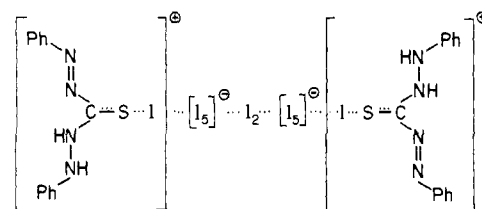


Figure 4. 2(Dithizone)-7(I₂)—schematic representation of the moiety structure found in the crystals.

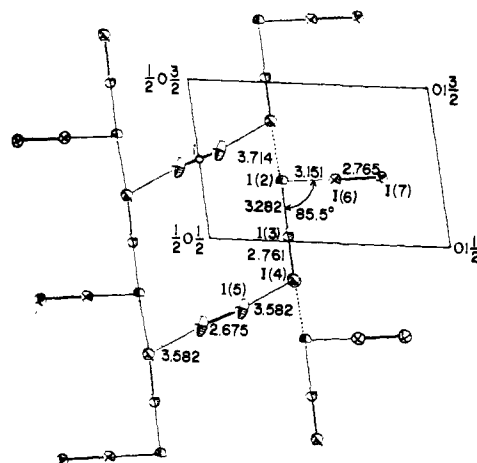


Figure 5. 2(Dithizone)-7(I₂)—diagrammatic sketch of the 12-membered ring of iodine atoms which form a repeating motif in the (210) planes.

The S(6)-C(3) and I(2)-I(3) vectors are approximately parallel and thus the 2(dithizone)-7(I₂) moiety is compact rather than extended. Because the distance between I(2) and S(6) is 5.7 Å and the dithizone fragment is bent away from the plane of the iodines ($\angle I(1)-S(6)-C(3) = 100.1^\circ$), there is space (in the crystal) for a dithizone fragment from another 2(dithizone)-7(I₂) moiety to intrude itself in the region between the reference dithizone molecule and the reference I(2)---I(3)-I(4) arm of the rhomboid unit of pattern in the iodine plane.

When distances between iodine atoms are taken into account, the fragment I(7)-I(6)-I(2)-I(3)-I(4) has a geometry similar to that of the discrete pentaiodide ion (in 2(valinomycin)-KI₃-KI₅²⁰ the I₅⁻ ion (symmetry C_{2v}-2) has dimensions I(7)-I(6) = 2.76, I(6)-I(2) = 3.08 Å, $\angle I(6)-I(2)-I(3) = 84^\circ$ (numbering has been changed to match that in Figure 3)). There are bridging iodine molecules (I(5)-I(5')) across the centers of symmetry which link the two "pentaiodide" fragments by secondary I(4)---I(5) interactions. Although I(2)-I(1) is formally an iodine molecule, the interatomic distance is the longest on record for such a species, and this is presumably a consequence of the strong S---I(1) interaction. On the other hand $d(I(5)-I(5'))$ is the same as that in gas-phase I₂,¹⁶ although the length in the crystal is perhaps underestimated as I(5) has a high Debye-Waller factor. Nevertheless this I₂ molecule has the shortest intramolecular distance so far encountered for I₂ in the solid state. A schematic representation is given in Figure 4.

All the iodine atoms except I(1) lie approximately in the (210) planes and are linked to translationally related groups in [001] directions by the secondary interactions I(2)---I(4') and I(2')---I(4); this leads to formation of 12-membered rings, nearly rhomboid in shape (Figure 5; sides of 9.839 and 9.757 Å and an interaxial angle of 112.9°). Similar 12-membered rings, with I₂ and I₃⁻ moieties as components, are found in diferrocenylselenium triiodide-iodine-hemi(methylene chloride),¹⁹ where the sides of the quasi-rhombus are 9.680 and 9.603 Å, respectively, and the

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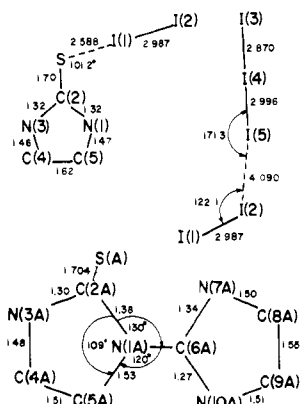


Figure 6. 1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium triiodide-(ethylenethiourea-diiodine)—dimensions of the constituent moieties. $d(\text{N}(1\text{A})-\text{C}(6\text{A})) = 1.35$ (2) Å. Average esds: $\sigma(\text{I}-\text{I}) \sim 0.002$, $\sigma(\text{I}-\text{S}) \sim 0.008$, $\sigma(\text{S}-\text{C}) \sim 0.02$ Å; $\sigma(\text{I}-\text{I}-\text{I}) \sim 0.01^\circ$, $\sigma(\text{I}-\text{I}-\text{S}) \sim 0.2^\circ$, $\sigma(\text{other angles}) \sim 2^\circ$.

interior angle of the rhombus is 100.5° .

The dithione-I(1) fragments protrude above and below these ribbons from their attachments at I(2) and I(2'), respectively. Parallel ribbons are offset along [010] with interleaving of dithione molecules. There are only van der Waals interactions between adjacent ribbons, both normal to the plane of the iodines and laterally.

1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium Triiodide-(Ethylenethiourea-Diiodine). The ethylenethiourea-I₂ moieties can be regarded as discrete units in which the mutual arrangement of ethylenethiourea and I₂ is very similar to those found in the other analogous interactions described in this paper. The iodines of I₂ are in the plane of the ethylenethiourea molecule, with $\tau(\text{N}(1)-\text{C}(2)-\text{S}-\text{I}(1)) = 0^\circ$. The cationic condensation product has its two five-membered rings almost coplanar, the angle between the plane through the imidazolidine-thione fragment (deviations from planarity < 0.024 Å) and the imidazolidinium fragment (deviations from planarity < 0.008 Å) being 3.3° . The overall dimensions are shown in Figure 6. The only I---I contact shorter than the sum of the van der Waals radii is between I₂ and I₃; $d[\text{I}(2)-\text{I}(5)] = 4.090$ (3) Å, which indicates only very weak interaction. The value of $\angle \text{I}-\text{I}-\text{I}$ is 122.1 (1) $^\circ$, rather different from the usual values of $\sim 175^\circ$ or $\sim 85^\circ$. The C⁺I₃⁻ and ethylenethiourea-I₂ moieties are segregated about alternate (200) planes.

Although the individual moieties in the crystal are achiral, their arrangement as a whole is chiral (space group $P2_1$); no attempt was made to determine the absolute configuration of the crystal used in the structure analysis. The orientation of the moieties in the crystal suggests appreciable polarity along [010].

Discussion

Features Common to These Five, and Other, Structures. Thione-Diiodine Interactions. The geometrical parameters found in the interaction of a thione group with a diiodine molecule are summarized in Table III. The values of $d(\text{S}-\text{I}(1))$ and $d(\text{I}(1)-\text{I}(2))$ fit a hyperbola rather well (Figure 7); two moieties without thione groups also fit this curve well. The claim^{8a} that the relation is linear is based on an insufficient number of data points. The values of $d(\text{C}=\text{S})$ do not appear to vary much despite the large variation in $d(\text{S}-\text{I}(1))$; however, the $d(\text{C}=\text{S})$ values are not accurate enough to warrant detailed discussion. The S---I(1)-I(2) arrangement is essentially linear, while $\angle \text{C}=\text{S}-\text{I}(1)$ varies from 110.0° to 95.6° , suggesting that the hybridization at S varies from sp³ to p, without any obvious relation to $d(\text{S}-\text{I}(1))$.

The torsion angles X-C=S---I(1) are either close to 0° (for the ethylenethiourea compounds) or to 90° (for the dithione compounds). A torsion angle of $\sim 0^\circ$ for the dithione compounds seems unlikely because it would lead to steric interaction between dithione and iodine atoms.

The series of molecular compounds listed in Table III can be considered as stages along the reaction coordinate between the

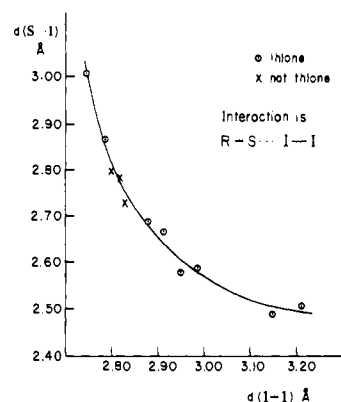
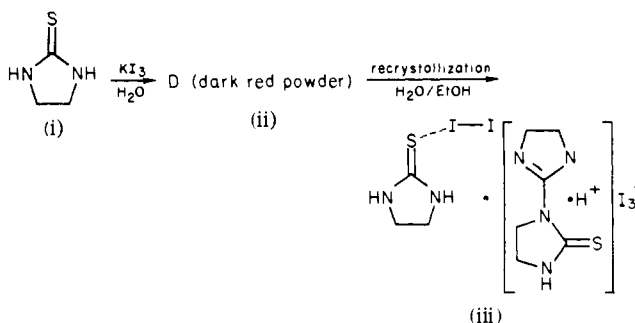


Figure 7. Variation of $d(\text{S}-\text{I})$ with $d(\text{I}-\text{I})$ for the structures listed in Table III.

Scheme I



¹H NMR (60 MHz, in Me₂SO-*d*₆; chemical shifts relative to Me₄Si)

(i) 3.48 (s)	(ii) 3.75 (s)	(iii) 3.53 (s)
7.85 (br s)	9.04 (br s)	3.69 (s)
		4.1-3.6 (m)
		8.92 } br
		9.53 } singlets
		10.40 } 1:2:1

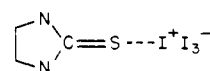
(ethylenethiourea)₂(I₂)₃, when measured in Me₂SO-*d*₆ solution, has resonances at 3.87 (s) and 9.52 ppm

separated neutral molecules RS and I₂ (for simplicity we mention only I₂ as the iodine species) and the ionic salt RSI⁺I₃⁻. Deep red-brown crystals of composition thiourea-I₂ have been prepared by Lin and Hope²³ but were too unstable for crystallographic analysis. Heterolytic fission of I₂ has been demonstrated²³ in bis(thiourea)iodine(1+) iodine [(NH₂)₂CSISC(NH₂)₂]⁺I⁻, but the dimeric cation is not analogous to the monomeric species we postulated above.

The salt-molecule molecular complex 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide-(ethylenethiourea-diiodine) appears to be the first example of cocrystallization of a charge-transfer iodine molecular compound with a polyiodide salt.

Polyiodide Moieties. The discussion in the previous section suggests that a useful first approximation to the structures of the compounds described in this paper can be based on predominance of the ionic contribution to the resonance hybrid. Thus dithione-I₂ would be essentially RSI⁺I₃⁻. Although this formulation for dithione-I₂ cannot be tested on the basis of measured bond lengths, the bond length test can be applied to the other structures and the results are remarkably good.

Ethylenethiourea-2(I₂) is written as



and the geometry of this unsymmetrical linear "triiodide" ion is compatible with those of true triiodide ions⁵—for example the

Foundation (BSF) for financial assistance. We thank Dr. M. Kapon for his help with computing.

Registry No. Dithizone- I_2 , 88995-88-4; ethylenethiourea- $2(I_2)$, 88995-89-5; 2(ethylenethiourea)- $3(I_2)$, 88995-90-8; 2(dithizone)- $7(I_2)$, 81615-07-8; 1-(1-imidazolyl)-2-thioximidazolidinium triiodide-(ethylenethiourea diiodide), 88995-91-9; ethylenethiourea, 96-45-7; di-

thizone, 60-10-6.

Supplementary Material Available: Tables of atomic parameters, anisotropic temperature factors, and observed and calculated structure factors are given for the five crystal structures reported (72 pages). Ordering information is given on any current masthead page.

Catalysis of Anilide Hydrolysis by Poly(ethylenimine) Derivatives

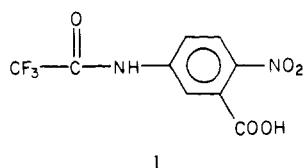
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Abstract: Amide hydrolysis in 4-nitro-3-carboxytrifluoroacetanilide (**1**) is catalyzed by poly(ethylenimines). The rate-controlling step is the formation of a tetrahedral intermediate, breakdown of which is catalyzed by the conjugate acid and base forms of the amine groups of the polymers. As estimated from the pH profiles of k_{cat} , the rate of hydroxide attack is 6-180 times greater in the polymer milieu than in bulk water. This enhancement in rate is largely a reflection of the increased local concentration of hydroxide in the vicinity of the cationic sites of the polymers; the hydrophobic local environments of the macromolecule appear to have little effect on the intrinsic reactivity of hydroxide ion. At low pH, water molecule attack on complexed anilide, **1**, is observed, and bound acetate, as a general base, assists therein.

Although micelle- or polymer-catalyzed reactions have been studied extensively,¹⁻³ successful estimation⁴⁻⁶ of the intrinsic reactivity of nucleophiles in micellar or polymeric domains relative to that in bulk water has been rare. In part this is because resolution of catalytic effects into contributions from enhanced intrinsic reactivity and from increased effective concentrations of the reactants has seldom been achieved. For reactions taking place in the apolar milieu of a polyelectrolyte, both the hydrophobicity and the electrostatic effects of the microenvironment can affect the intrinsic reactivity as well as the effective concentrations of the reactants. In addition, perturbation in the ionization of species involved in the catalyzed reactions further complicates analysis of the kinetic results.

Many derivatized micelles or polymers have been used as catalysts for ester hydrolysis, and the results have been frequently compared with the actions of proteases. Although amides are the natural substrates of the proteases, their hydrolysis has seldom been investigated in micellar or polymeric systems, due to the much greater stability of amide bonds compared with ester bonds. In this article, kinetic results in the hydrolysis of 4-nitro-3-carboxytrifluoroacetanilide (**1**) catalyzed by various poly(ethy-



lenimine) (PEI) derivatives are reported. As the amide hydrolysis of **1** occurs through the attack of hydroxide ion, the enhanced rates

have been analyzed in terms of the intrinsic reactivity and the effective concentration of hydroxide ion in the hydrophobic milieu of the cationic polymers. Contributions of other catalytic factors have also been evaluated.

Experimental Section

Materials. 4-Nitro-3-carboxytrifluoroacetanilide was prepared from 2-nitro-5-aminobenzoic acid (0.5 g) and trifluoroacetic anhydride (5 mL) by stirring the mixture at room temperature overnight. The crystals that formed were filtered, washed with petroleum ether, and recrystallized from ether-petroleum ether: mp 217-221 °C dec. Anal. Calcd for $C_9H_5F_3N_2O_5$: C, 38.86; H, 1.81; N, 10.07. Found: C, 38.94; H, 1.98, N, 10.09.

Modifications of poly(ethylenimine) (PEI) was carried out according to literature procedures.⁷⁻⁹ The sample of polymer used, PEI 600 (Dow Chemical Co.), contains, on the average, 1400 monomer residues per macromolecule. Of these, 25% provide primary amino groups, 50% secondary, and 25% tertiary. Lauryl groups become attached preferentially to the primary nitrogens and 4-imidazolylmethyl groups are linked mainly to the secondary nitrogens. The modified polymers were purified by ultrafiltration against 0.1 M NaCl and then against water.

The poly(ethylenimine) derivatives prepared had the following stoichiometric compositions: $La_{12}PEI$, $(C_{12}H_{25})_{0.12m}(C_2H_4N)_{1.0m}(Cl)_{0.54m}$; $La_{12}Im_{10}PEI$, $(C_{12}H_{25})_{0.12m}(4\text{-imidazolylmethyl})_{0.10m}(C_2H_4N)_{1.0m}(Cl)_{0.50m}$; $La_{25}PEI$, $(C_{12}H_{25})_{0.25m}(C_2H_4N)_{1.0m}(Cl)_{0.50m}$; $La_{25}Me_QPEI$, $(C_{12}H_{25})_{0.25m}(CH_3)_{1.45m}(C_2H_4N)_{1.0m}(Cl)_{0.70m}$; m is 1400.

Buffer Solutions. Since the kinetic behavior of the reactions catalyzed by poly(ethylenimine) derivatives is influenced by the nature and concentrations of anions present, buffer solutions were prepared as follows. For monoamine buffers [3-(cyclohexylamino)-1-propanesulfonic acid (Caps) at pH 9.5-11, tris(hydroxymethyl)aminomethane (Tris) at pH 7.5-9, bis(2-hydroxyethyl)aminotris(hydroxymethyl)methane (Bistris) at pH 5.5-7], the base (0.02 M) was first neutralized in solution with hydrochloric acid or with acetic acid to yield a 1:1 salt, a desired amount of polymer was added, and then the pH of the solution was adjusted with sodium hydroxide. At pH 4-5.5, three other buffer systems were used. When chloride was to be the anion, 0.02 M methoxyamine hydrochloride

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