

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 photolysis 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, β = 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, α = 105.1 (1)°, β = 81.0 (1)°, γ = 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, α = 116.9 (1)°, β = 72.5 (1)°, γ = 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, α = 101.8 (1)°, β = 87.1 (1)°, γ = 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, β = 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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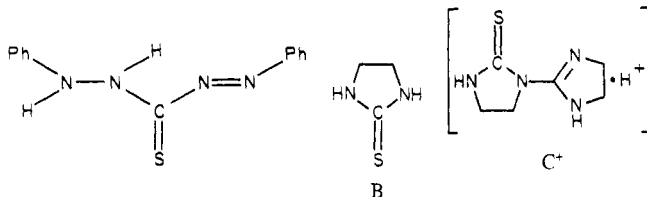
Table I. Crystal Data

	dithizone-I ₂	ethylenethiourea-2(I ₂) ^c	2(ethylenethiourea)-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-diphenylthiocarbazone) 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)·I₂·I₂·(I) chain found in A₂·(I₂)₇.¹⁰

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

	2(ethylene thiourea)-3(I ₂)	2(triphenyl- phosphine 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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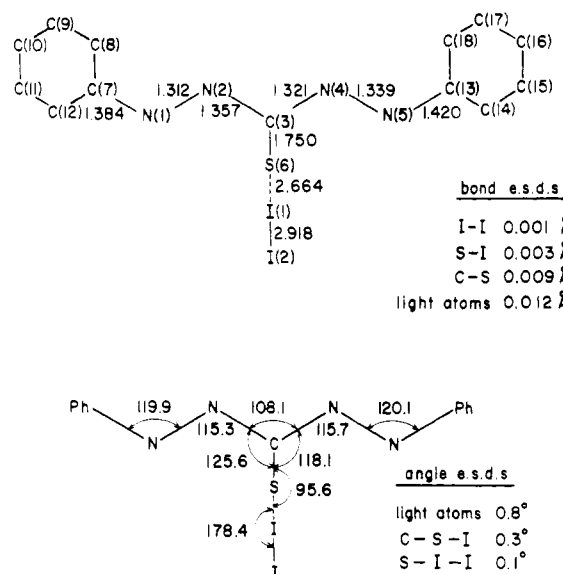
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Table III. Geometrical Parameters for Interaction of Thione Group with the Diiodine Molecule^a

moiety	$X_2C=S \cdots I(1)-I(2)$					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)	b
2(dithizone)-7(I ₂)	2.506 (8)	3.215 (3)	179.1 (2)	100.4 (5)	83.4 (1.7)	b
2(ethylenethiourea)-3(I ₂)	2.580 (7)	2.984 (3)	177.5 (2)	102.8 (9)	3.7 (2.6)	b
ethylenethiourea-I ₂ in $(C^+I_3^-) \cdot A \cdot I_2$	2.588 (8)	2.987 (2)	178.2 (2)	101.2 (4)	6.8 (2.5)	b
dithizone-I ₂	2.664 (3)	2.918 (1)	178.4 (1)	95.6 (3)	78.5 (6)	b
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) 107.0 (1)		81
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
2(merocyanine)-I ₂	3.098 (5)	2.750 (1)	178.4 (1)	99.5 (7)	76.8 (1.0)	9

^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 S₇I⁺ 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 $[C^+I_3^-] \cdot [B \cdot I_2]$. 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

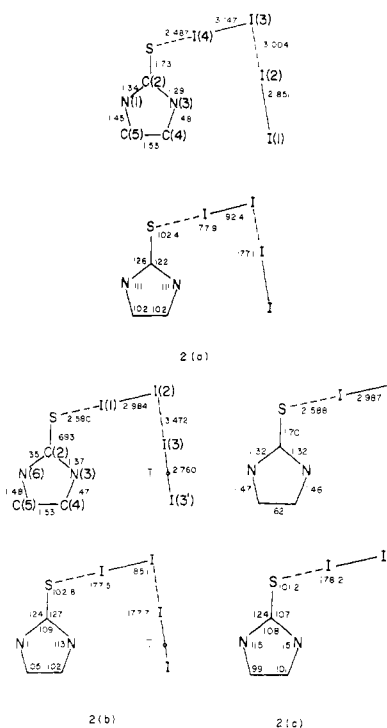


Figure 2. Bond lengths and angles in moieties involving ethylenethiourea and iodine: (a) ethylenethiourea-2(I₂), (b) 2(ethylenethiourea)-3(I₂), (c) ethylenethiourea-I₂ in the salt-molecule complex $(C^+I_3^-) \cdot (A \cdot I_2)$. In these and other analogous diagrams, the formally secondary interactions 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 $\angle C-S \cdots I = 95.6 (3)^\circ$. 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

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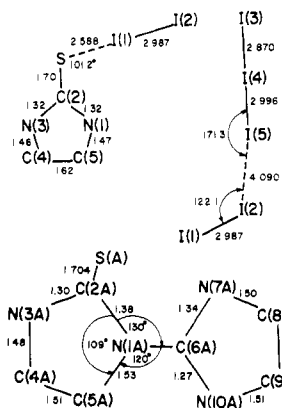


Figure 6. 1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium triiodide—(ethylenethiourea-diiodide)—dimensions of the constituent moieties. $d(\text{N}(1\text{A})\text{---C}(6\text{A})) = 1.35$ (2) Å. Average esds: $\sigma(\text{I---I}) \sim 0.002$, $\sigma(\text{I---S}) \sim 0.008$, $\sigma(\text{S---C})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

interior angle of the rhombus is 100.5° .

The dithizone-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 dithizone 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 $\tau(\text{N}(1)\text{---C}(2)\text{---S---I}(1)) = 0^\circ$. 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 $<0.024 \text{ \AA}$) and the imidazolidinium fragment (deviations from planarity $<0.008 \text{ \AA}$) 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⁻; $d[\text{I}(2)\text{---I}(5)] = 4.090(3) \text{ \AA}$, which indicates only very weak interaction. The value of $\angle \text{I---I---I}$ 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 $\text{S} \cdots \text{I}(1)-\text{I}(2)$ arrangement is essentially linear, while $\angle \text{C}=\text{S} \cdots \text{I}(1)$ varies from 110.0° to 95.6° , suggesting that the hybridization at S varies from sp^3 to p, without any obvious relation to $d(\text{S} \cdots \text{I}(1))$.

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

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

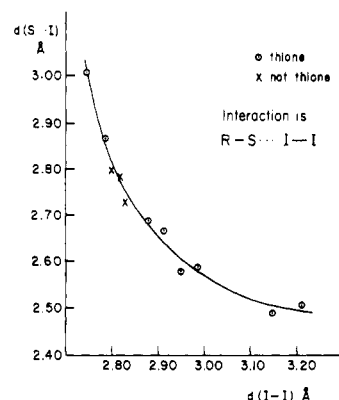
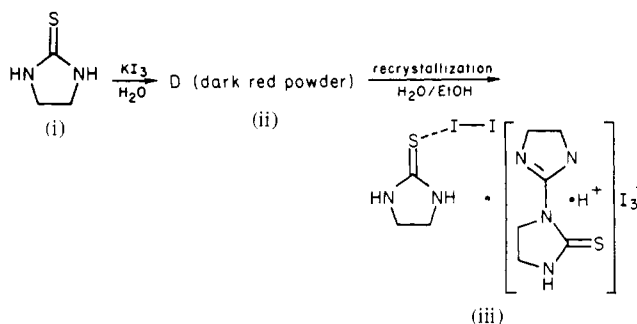


Figure 7. Variation of $d(\text{S--I})$ with $d(\text{I--I})$ for the structures listed in Table III.

Scheme 1

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

(i) 3.48 (s)
7.85 (br s)

(ii) 3.75 (s)
9.04 (br s)

(iii) 3.53 (s)
3.69 (s)
4.1–3.6 (m)
8.92 } br
9.53 } singlets
10.40 } 1:2:1

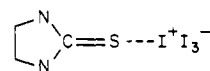
(ethylenethiourea)₂(I₂)₃, when measured in Me₂SO-*d*₆ solution, has resonances at 3.87 (s) and 9.52 ppm

separated neutral molecules RS and I_2 (for simplicity we mention only I_2 as the iodine species) and the ionic salt RSI^+I^- . Deep red-brown crystals of composition thiourea- I_2 have been prepared by Lin and Hope²³ but were too unstable for crystallographic analysis. Heterolytic fission of I_2 has been demonstrated²³ in bis(thiourea)iodine(1+) iodine $[(NH_2)_2CSISC(NH_2)_2]^+I^-$, 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.

Polyiodine 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 dithizone- I_2 would be essentially RSI^+I^- . Although this formulation for dithizone- I_2 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

(23) Lin, G. H.-Y.; Hope, H. *Acta Crystallogr., Sect. B* **1972**, *28*, 643–646.

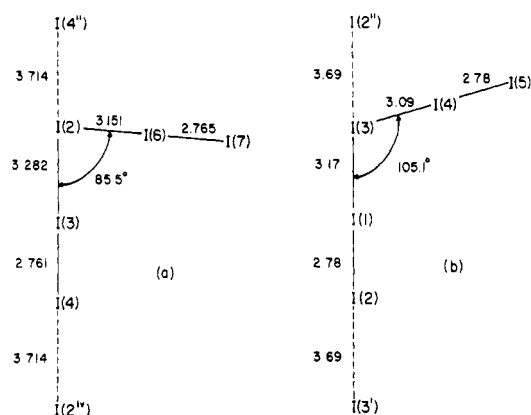
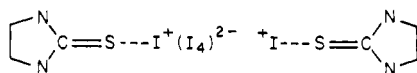


Figure 8. Comparison of the geometries of fragments of the iodine arrangements in (a) 2(dithizone)-7(I₂) and (b) 4(benzophenone)-LiI₅.²⁵

overall length is 5.85 Å, very close to the values found for most symmetrical and unsymmetrical I₃⁻ ions.

2(Ethylenethiourea)-3(I₂) can be written as



and the dimensions of the "tetraiodide" ion fit the range of known values,²¹ although here the outer I---I distance is ~0.1 Å longer than found previously. Another point of resemblance is that I₄²⁻ ions appear to require stabilization by interaction with neighboring groups in the crystal.

We have already noted above that 2(dithizone)-7(I₂) can be written as RSI⁺(I₅)-(I₂)-(I₅)⁻ISR (Figure 4). One part of this structure has a striking resemblance to the chain of I₅⁻ ions found in the clover salt (benzophenone)₄LiI₅.^{24,25} The relevant dimensions are compared in Figure 8, the only appreciable difference being in the value of the I-I-I angle.

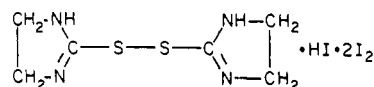
The geometry of the rather weak interaction between I₃⁻ and I₂ moieties in the salt-molecule molecular complex [C⁺I₃⁻]-[B·I₂] (see Figure 6) does not suggest incipient formation of either I₄²⁻ or I₅⁻ ions; instead there is some resemblance to the T-shaped disposition of neighboring I₃⁻ ions found in 4(glycine)-KI₃ and other triiodides.²⁶

Organic Moieties. The accuracy with which the positions of the C and N atoms were determined is limited because the diffraction patterns are dominated by the scattering from the iodine atoms; a fortiori hydrogen positions were not determined at all. Thus no conclusions can be drawn from the similarity of the dimensions found for the ethylenethiourea moiety in the various compounds described here (and in crystalline ethylenethiourea itself²⁷), nor has it been possible to establish the location of hydrogen atoms in the dithizone moieties (or whether there is disorder). Dimensions have been reported for the dithizone molecule in dithizone itself²⁸ and in dithizone-I₂ and 2(dithizone)-7(I₂). In all three instances the molecule exists in the extended anti, s-trans configuration.²⁹⁻³¹ The bond lengths, if taken at face value, would suggest that the molecule is 1,5-diphenylthiocarbodiazone (i.e., C₁₃H₁₀N₄S instead of C₁₃H₁₂N₄S), but mass spectrometric molecular weight measurements³² confirm the accepted C₁₃H₁₂N₄S

composition. Laing²⁸ has assigned the hydrogens in dithizone to the two outer nitrogens of the chain; we believe that stronger evidence is needed (Laing's crystals scattered poorly) before the accepted canonical formula for dithizone is abandoned. The current situation appears to be that none of the three determinations of molecular geometry for dithizone is accurate enough to allow bond orders to be inferred from bond lengths.

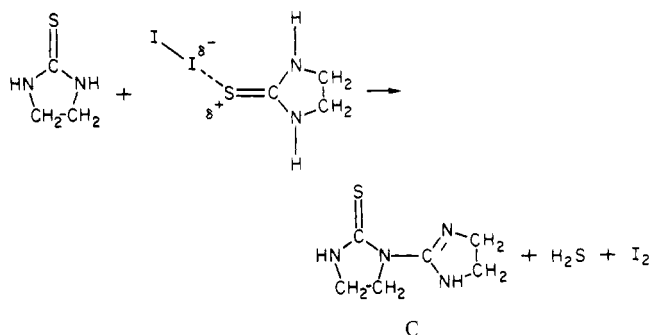
The 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium cation is planar; in particular the distribution of atoms around N(1A) is planar, which would appear to eliminate this position as a possible protonation site. Furthermore the bond lengths and angles are similar to those found in ethylenethiourea. Thus there appears to be considerable delocalization of positive charge; possible protonation sites are N(3A), N(7A) (amine groups in both examples), or S.

Johnson-Edens Reaction. Johnson and Edens¹³ reacted ethylenethiourea with KI + I₂ in water and formulated the (red crystalline) product as



In our repetition of this reaction, we observed, as they did, that the formation of the red crystals occurs in two steps (Scheme 1). It seems unlikely that the dimeric pentaiodide they propose should rearrange to our crystalline product under the comparatively mild conditions of recrystallization. It seems much more likely that a polyiodine species is formed, which partially undergoes condensation during recrystallization. More rigorous conditions, such as digestion with boiling water for 45 min, will complete the reaction, yielding exclusively C as its hydroiodide salt.

The formation of C could occur as follows, with the Lewis acid I₂ acting as a catalyst:



The neutral product is facily protonated in the presence of acid. We emphasize, as did Johnson and Edens, that the condensation product is not the primary product of the reaction but a secondary product. In the original synthesis of Jaffé and Kühn,³³ ethylenethiourea is first formed from ethylenediamine and thiophosgene, and this then further condenses to give C.

Acknowledgment. Dr. Schwotzer thanks the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung for a postdoctoral bursary. We are also grateful to the Deutsche Forschungsgemeinschaft and the U.S.-Israel Binational Science

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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-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide-(ethylenethiourea diiodide), 88995-91-9; ethylenethiourea, 96-45-7; dithizone, 60-10-6.

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

Junghun Suh and Irving M. Klotz*

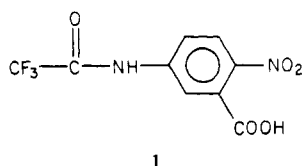
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received August 22, 1983

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-

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



1

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

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: $La_{12}PEI$, $(C_{12}H_{25})_{0.12m}(C_2H_4N)_{1.0m}(Cl)_{0.54m}$; $La_{12}Im_{10}PEI$, $(C_{12}H_{25})_{0.12m}(4\text{-imidazolylmethyl})_{0.10m}(C_2H_4N)_{1.0m}(Cl)_{0.50m}$; $La_{25}PEI$, $(C_{12}H_{25})_{0.25m}(C_2H_4N)_{1.0m}(Cl)_{0.50m}$; $La_{25}MeQPEI$, $(C_{12}H_{25})_{0.25m}(CH_3)_{1.45m}(C_2H_4N)_{1.0m}(Cl)_{0.70m}$; 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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