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Reactions of Imidazole-2-thiones with Molecular Iodine and the Structures of Two Crystalline Modifications of the 1:1 1,3-Dimethylimidazole-2-thione–Diiodine Charge-Transfer Complex ($C_5H_8I_2N_2S$)[1]

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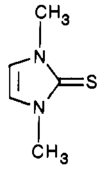
Abstract: Imidazole-2-thione, 1-methylimidazole-2-thione, and 1,3-dimethylimidazole-2-thione (**1**) react with diiodine to give 1:1 charge-transfer complexes. Both charge-transfer and blue-shifted iodine bands are observed in the complexes. A 1-equiv portion of 1,3-dimethylimidazole-2-thione (**1**) reacts with 1 equiv of diiodine in dichloromethane to give a charge-transfer complex (α, **7**) that contains the planar 6π electron aromatic imidazolium system. The thione **1**–diiodine charge-transfer complex **7** (α) is monoclinic [$a = 9.6001$ (20) Å, $b = 10.2196$ (23) Å, $c = 11.1070$ (21) Å, $\beta = 102.112$ (15)°, $V = 1065.6$ (4) Å^3, $Z = 4$, space group $P2_1/n$, $R_F = 0.045$, $R_{wF} = 0.067$]. In the presence of excess thione **1**, a different crystalline modification (β, **8**) of charge-transfer complex **7** is formed. Structure **8** is monoclinic [$a = 6.9435$ (6) Å, $b = 8.5462$ (7) Å, $c = 9.1811$ (8) Å, $\beta = 91.790$ (7)°, $V = 544.6$ (1) Å^3, $Z = 2$, space group $P2_1/m$ (No. 11; C_{2h}^2), $R_F = 0.030$, $R_{wF} = 0.048$]. The major difference between crystal modifications **7** and **8** is the orientation of the iodine unit relative to the ring system.

Although 1,3-dimethylimidazole-2-thione (1,3-dihydro-1,3-dimethyl-2*H*-imidazole-2-thione, 1,3-dimethyl-2-thioxo-1,2-dihydroimidazole, **1**)[4-6] reacts with dibromine to give dication disulfide **2** [2,2′-dithiobis(1,3-dimethyl-4-imidazolin-2-ylium) dibromide], with dibromide, dichlorine, and iodine monobromide to give stable hypervalent tricoordinate tricovalent sulfuranes **3** (e.g. 1,3-dimethyl-4-imidazolin-2-ylium dibromo-λ^4-sulfanide), and cyanogen chloride to give salts **4**,[7-11] the structure of the thione **1**–diiodine charge-transfer complex has not been elucidated.[1,12-17]



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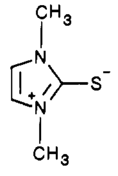

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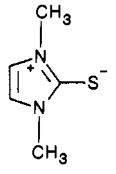

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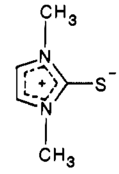

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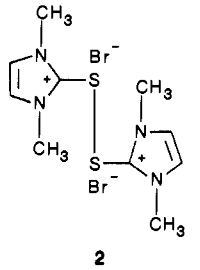

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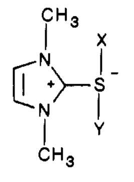
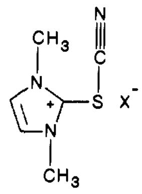
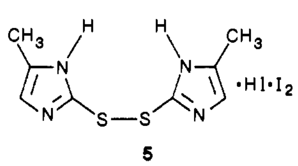


3a: X = Y = Br
b: X = Y = Cl
c: X = Br; Y = I



4a: X = Br
b: X = Cl

Periodide **5** has been reported as the product from the reaction of 4-methylimidazole-2-thione and aqueous diiodine–potassium iodide,[18] and disulfide **6** was obtained from the reaction of 4(or 5)-carbethoxy-5(or 4)-methylimidazole-2-thione and aqueous diiodine.[19-22]



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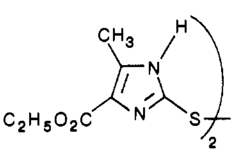

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The nature of charge-transfer complexes between heterocyclic antithyroid drugs and diiodine is an important area of interest in the study of hyperthyroidism,[13] and the electrical properties in general and the superconducting ability in particular of sulfur–iodine complexes are also of current interest.[23] In this report we describe the structures of two crystalline modifications (α, **7**;

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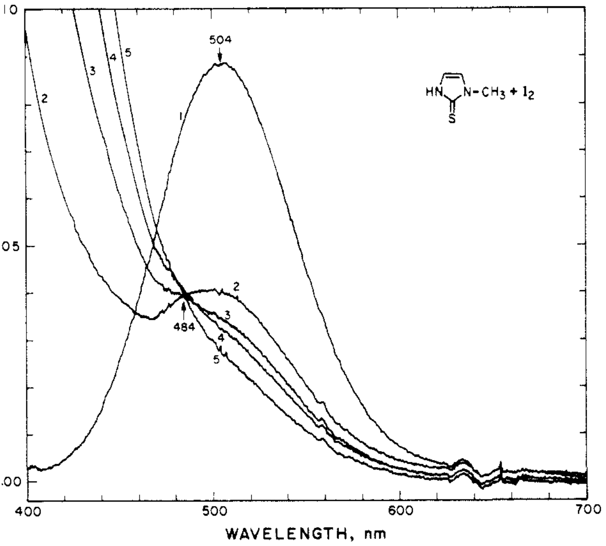


Figure 1. Effects of varying 1-methylimidazole-2-thione concentration on the absorption spectra of the thione–diiodine charge-transfer complex in CH_2Cl_2: $[I_2] = 1.0 \times 10^{-4}$ M. Concentration of thione: (1) 0.0, (2) 2.0×10^{-5} M, (3) 5.0×10^{-5} M, (4) 7.0×10^{-5} M, (5) 10.0×10^{-5} M.

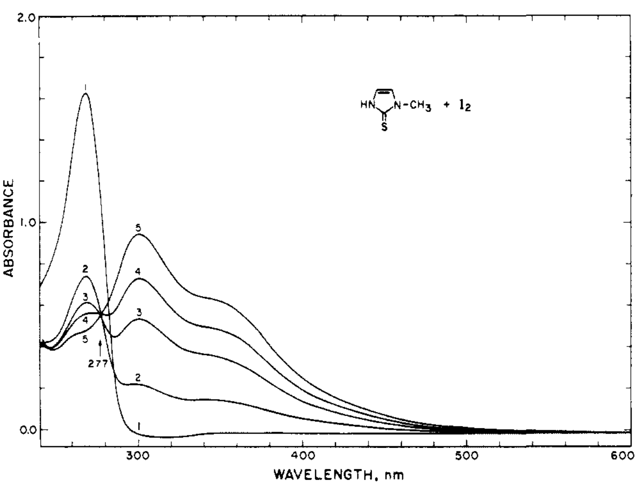


Figure 2. Effects of varying diiodine concentration on the absorption spectra of the 1-methylimidazole-2-thione–diiodine charge-transfer complex in CH_2Cl_2: [thione] = 1.0×10^{-4} M. Diiodine concentration: (1) 0.0, (2) 2.0×10^{-5} M, (3) 5.0×10^{-5} M, (4) 7.0×10^{-5} M, (5) 10.0×10^{-5} M.

β, **8**) of the 1:1 1,3-dimethylimidazole-2-thione (**1**)–diiodine charge-transfer complex and properties of the 1:1 thione–diiodine charge-transfer complexes from imidazole-2-thione and 1-methylimidazole-2-thione.

We have investigated the interaction between imidazole-2-thione, 1-methylimidazole-2-thione, and 1,3-dimethylimidazole-2-thione (**1**) and diiodine via conventional ultraviolet–visible spectrometry and spectrophotometric stopped-flow techniques.[1] Although the rates of charge-transfer complex formation were too fast to be followed by stopped-flow techniques, the stoichiometry (1:1) of the thione–diiodine charge-transfer complexes was determined by Job's method of continuous concentration variation.[24] Formation constants [K_c(298 K)] for the thione **1**–diiodine charge-transfer complex in dichloromethane (106 905 L mol^{-1}) and the tetrachloromethane (27 096 M^{-1}) have been reported.[12,13,25]

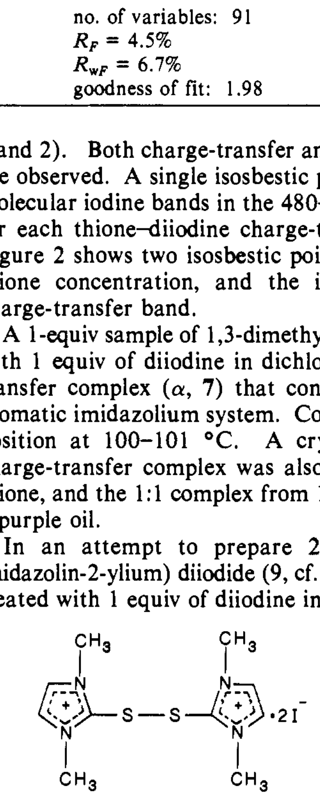
Spectra of the thione–diiodine charge-transfer complexes in dichloromethane at 24 °C were taken from 240 to 800 nm (Figures 1 and 2). Both charge-transfer and blue-shifted diiodine bands are observed. A single isosbestic point between complexed and molecular iodine bands in the 480–490-nm region was observed for each thione–diiodine charge-transfer complex (Figure 1). Figure 2 shows two isosbestic points, the effects of decreasing thione concentration, and the increase in intensity of the charge-transfer band.

Table I. Experimental Data for the X-ray Diffraction Study of Crystal Modification **7** (α, $C_5H_8I_2N_2S$)

formula: $C_5H_8N_2SI_2$
fw: 382.0
crystal system: monoclinic
space group: $P2_1/n$
$a = 9.6001$ (20) Å
$b = 10.2196$ (23) Å
$c = 11.1070$ (21) Å
$\beta = 102.112$ (15)
$V = 1065.6$ (4) Å^3
$Z = 4$
D_{calcd}, g/cm^3 = 2.38
diffractometer: Nicolet P3
data collected: $+h,+k,\pm l$
scan type: coupled θ(crystal)-2θ(counter)
scan width: $[2\theta(K\alpha_1) - 1.2] \rightarrow [2\theta(K\alpha_2) + 1.2]$
scan speed: 4.0 deg min^{-1} (in 2θ)
$2\theta_{max}$, deg: 60.0
μ(Mo Kα), cm^{-1} = 59.8
no. of unique reflections: 3138
no. of reflections with $I > 1.5\sigma(I)$: 2433
no. of variables: 91
$R_F = 4.5\%$
$R_{wF} = 6.7\%$
goodness of fit: 1.98

A 1-equiv sample of 1,3-dimethylimidazole-2-thione (**1**) reacts with 1 equiv of diiodine in dichloromethane to give a charge-transfer complex (α, **7**) that contains the planar 6π electron aromatic imidazolium system. Compound **7** melts with decomposition at 100–101 °C. A crystalline 1:1 thione–diiodine charge-transfer complex was also obtained from imidazole-2-thione, and the 1:1 complex from 1-methylimidazole-2-thione is a purple oil.

In an attempt to prepare 2,2′-dithiobis(1,3-dimethyl-4-imidazolin-2-ylium) diiodide (**9**, cf. **2**),[26,27] 2 equiv of thione **1** was treated with 1 equiv of diiodine in dichloromethane. Removal of solvent gave a solid (mp 105–106 °C dec) that analyzed for a 2:1 thione **1**–diiodine complex ($C_{10}H_{16}I_2N_4S_2$) and was *tentatively* assigned structure **10** [bis(1,3-dimethylimidazole-2-thione)iodine(I) iodide].[28-30] Attempts to grow crystals of the 2:1 thione **1**–diiodine complex (**10**) by the method of liquid dif-



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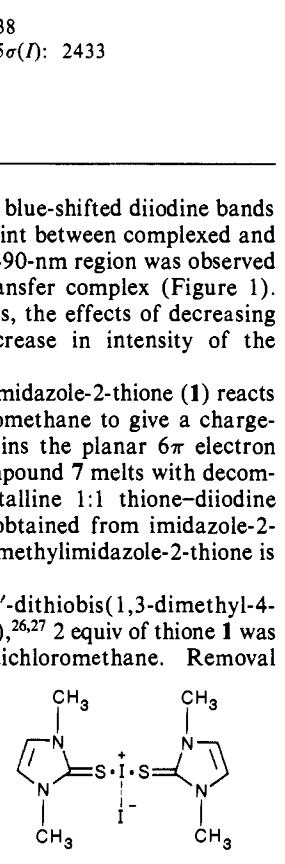

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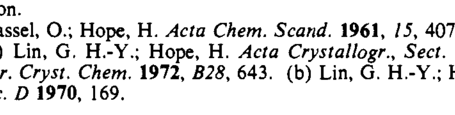
[26] 1,3-Diphenylimidazole-2-thione reacts with trifluoromethanesulfonic anhydride to form a stable dication disulfide.[27]



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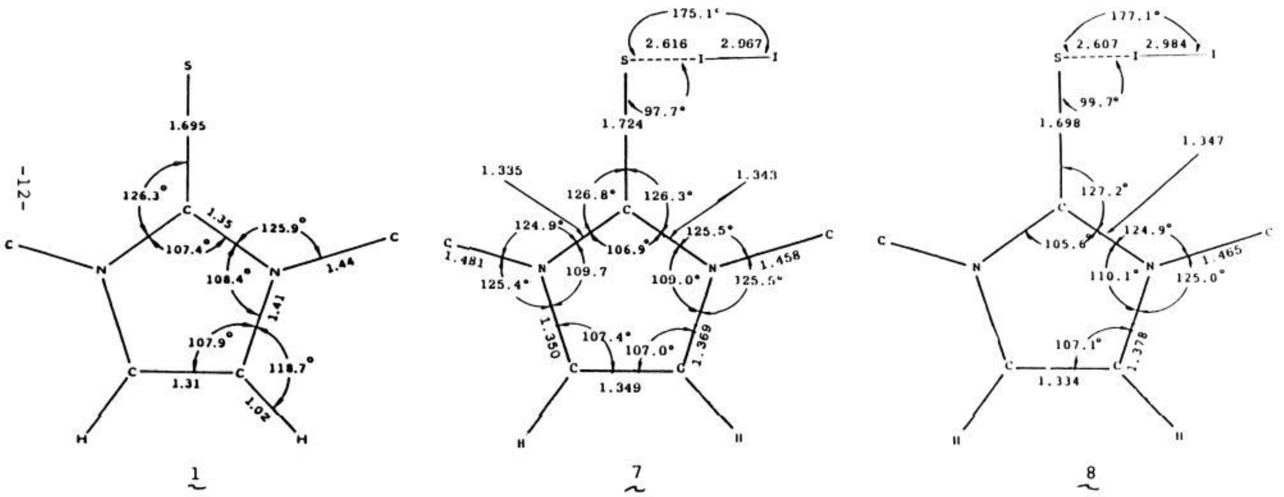


Figure 3. Comparison of the interatomic distances (angstroms) and interatomic angles (degrees) in thione **1**[4] and in crystal modifications **7** (α) and **8** (β) of the 1,3-dimethylimidazole-2-thione (**1**)–diiodine complex.

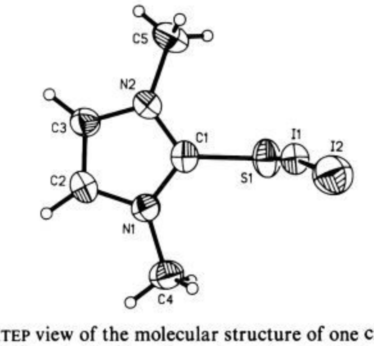


Figure 4. ORTEP view of the molecular structure of one crystalline form (α, **7**) of the thione **1**–diiodine charge-transfer complex. Thermal ellipsoids are drawn at the 30% probability level.

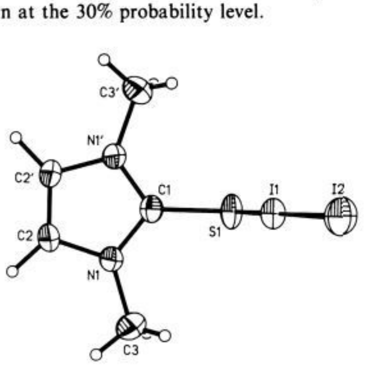


Figure 5. ORTEP view of the molecular structure of one crystalline form (β, **8**) of the thione **1**–diiodine charge-transfer complex. Thermal ellipsoids are drawn at the 30% probability complex.

fusion [dichloromethane–petroleum ether (30–60 °C)] for X-ray structure determination gave noncomplexed thione **1** and a 1:1 thione **1**–diiodine charge-transfer complex (β, **8**; mp 117–118 °C dec). Charge-transfer complex **8** is a different crystal modification (β) of the 1:1 thione **1**–diiodine complex **7** (α).

Figure 3 shows a comparison of the interatomic distances and bond angles in thione **1**,[4] in crystal modification **7** (α), and in crystal modification **8** (β). ORTEP views of crystalline modifications **7** and **8** are shown in Figures 4 and 5, respectively. Stereoscopic views of the molecular packing in the two crystalline modifications (**7**, **8**) of the thione **1**–diiodine charge-transfer complex are seen in Figures 6 and 7. Tables I and II give experimental data from the X-ray diffraction study of crystal modifications **7** and **8** of the thione **1**–diiodine charge-transfer complex.

Thione **1** is a planar molecule in which the lone-pair electrons on the nitrogen atoms can be envisaged as overlapping with the p orbital of the thiocarbonyl carbon atom, giving the resonance structures **1b** and **1c**. Bond angles and bond lengths in Figure 3 clearly indicate that structures **1b** and **1c** are major contributors to resonance hybrid **1d**.[4] Polar solvents favor the charge-separated structures **1b** and **1c** and hence the formation of the charge-transfer (donor–acceptor) complex **7** or **8**.

Table II. Experimental Data for the X-ray Diffraction Study of Crystal Modification **8** (β, $C_5H_8I_2N_2S$)

formula: $C_5H_8N_2SI_2$
fw: 382.0
crystal system: monoclinic
space group: $P2_1/m$ (No. 11; C_{2h}^2)
$a = 6.9435\ (6)$ Å
$b = 8.5462\ (7)$ Å
$c = 9.1811\ (8)$ Å
$\beta = 91.790\ (7)$
$V = 544.6\ (1)$ Å^3
$Z = 2$
D_{calcd}, g/cm^3 = 2.33
diffractometer: Nicolet P3
data collected: $+h,+k,\pm l$
scan type: coupled θ(crystal) − 2θ(counter)
scan width: $[2\theta(K\alpha_1) - 1.2] \rightarrow [2\theta(K\alpha_2) + 1.2]$
scan speed: 4.0 deg min^{-1} (in 2θ)
$2\theta_{\max}$, deg: 55.0
μ(Mo Kα), cm^{-1} = 58.5
no. of unique reflections: 1338
no. of reflections with $I > 1.5\sigma(I)$: 1233
no. of variables: 52
$R_F = 3.0\%$
$R_{wF} = 4.8\%$
goodness of fit: 1.51

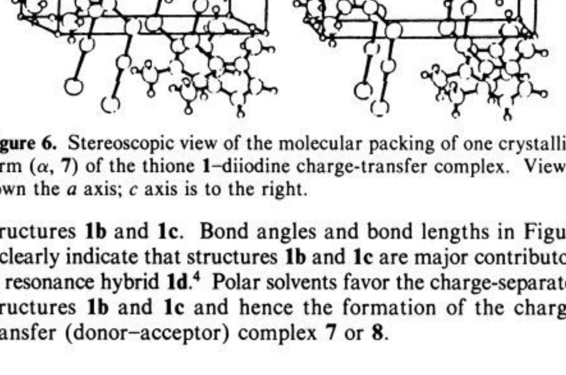
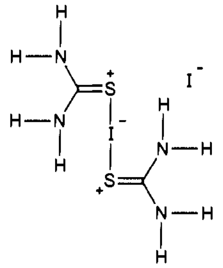


Figure 6. Stereoscopic view of the molecular packing of one crystalline form (α, **7**) of the thione **1**–diiodine charge-transfer complex. View is down the a axis; c axis is to the right.

Figure 3 shows that each crystalline modification (**7**, **8**) of the 1:1 thione **1**–diiodine charge-transfer complex contains a planar 6π electron aromatic imidazolium system. The lengthening of the olefinic double bond and shortening of the carbon–nitrogen bonds further demonstrate formation of a delocalized aromatic bond system (6π electrons) in the thione **1**–diiodine charge-transfer complex (**7**, **8**). Additional evidence for partial double-bond character is seen in the lengthening of the C═S bond in **7** and shortening of the two adjacent carbon–nitrogen bonds in **7** and **8**. The C-S bond distances of 1.724 (6) and 1.698 (6) Å in the α (**7**) and β (**8**) modifications, respectively, are greater than the C═S value of 1.61 Å and shorter than the C—S single-bond value of 1.81 Å.[31-34] The average C-S distance of 1.711 (18) Å is comparable to that found in bis(thiourea)iodine(I) iodide (**11**), in which the C-S bond is 1.724 (5) Å.[30a,b] A lengthening effect, similar to the above, has been observed for the P-S bond in bis(triphenylphosphine sulfide-*S*-iodine-1)iodine (**12**).[35]



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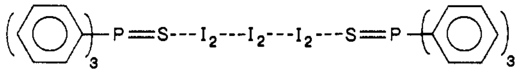

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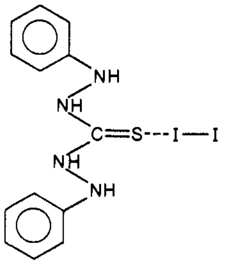
The C-S-I angles of 97.7 (2)° (α form, **7**) and 99.7 (2)° (β form, **8**) lie in the normal range of 92–110° [e.g., and C═S—I in 1,5-diphenylthiocarbazone iodide (dithizone–I_2, **13**) is 95.6 (3)°].[17b] The average S-I distance of 2.612 (6) Å is larger than the sum of the single-bond covalent radii (2.37 Å) for sulfur and iodine, indicating that the thiocarbonyl group becomes more polar (cf. **1b**, **1c**) as electrons are donated from sulfur into the lowest unoccupied antibonding molecular orbital of diiodine.[14,15,36] A comparison of shortened S-I distances to the lengthened I-I average distance [2.976 (12) Å] also indicates in the thione **1**–diiodine complex that thione **1** is a strong donor to diiodine. This is in accord with comparisons of S-I and I-I interactions among other thione–diodine complexes.[17b] Weaker S-I interactions in bis(triphenylphosphine sulfide) tridiiodine (**12**) [d(S-I) = 2.729 (2) Å] and stronger S-I interactions in bis(ethylenethiourea) tridiiodine (**14**) [d(S-I) = 2.580 (7) Å] are accompanied by the corresponding shorter I-I distance of 2.838 (1) Å in bis(triphenylphosphine sulfide) tridiiodine (**12**) and the longer I-I distance of 2.984 (3) Å in bis(ethylenethiourea) tridiiodine (**14**). The I-I distances in both the α [**7**; d(I-I) = 2.967 (1) Å] and β [**8**; d(I-I) = 2.984 (1) Å] modifications of the thione **1**–diiodine charge-transfer complex are longer than the I-I bond distance in the gas phase (2.677 Å)[37] and in crystalline diiodine (2.715 Å) at 110 K.[38]



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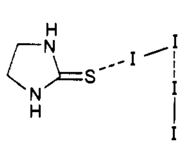
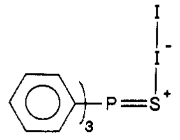


14

It is also of interest to compare properties of arsine sulfide–diiodine complexes (R_3AsS-I_2),[39] phosphoryl sulfide–diiodine complexes (R_3PS-I_2, **15**),[35,40,41] and sulfur (**11**, cf. **2**, 9, **10**)[30] analogues. Equilibrium constant values for 1:1 charge-transfer complexes are greater for thiourea–diiodine adducts (**11**) than for phosphoryl sulfide–diiodine complexes (**15**).[15] The $-\Delta H°$ values (8.6–12.8 kcal mol^{-1}) for arsine sulfide–diiodine complexes suggest that the Lewis basicity of the R_3AsS donor is slightly greater than that of the R_3PS donor.[39]



15

The S-I-I linkages are nearly linear with angles of 175.1 (1)° (α form, **7**) and 177.11 (4)° (β form, **8**). In both modifications, the rings are planar and perpendicular to the planes defined by C(1)-S(1)-I(1). The torsion angles N-C-S-I are 90° (α) and 92.6° (β). In the α form (**7**), I(2) is displaced from the C(1)-S(1)-I(1) plane by 0.253 Å. In the β form (**8**), however, all four atoms must lie on the mirror plane at $y = {}^1/_4$.

Close intermolecular contacts are observed for both the α (**7**) and β (**8**) modifications of the 1,3-dimethylimidazole-2-thione-diiodine complex. In the α form (**7**), the molecules pack in an interleaving geometry (Figure 6). The closest intermolecular contacts occur between the center iodine, I(1), and the hydrogen atoms near the plane of the imidazole ring. I(1) $(\bar{x}, \bar{y}, \bar{z})$ is 3.27 and 3.19 Å from H(2A) and H(4C), respectively. Similar interactions are observed between iodine atoms and hydrogen atoms near the plane of the thiourea ring in bis(thiourea)iodine(I) iodide (**11**).[30a,b] The closest nonhydrogen contact is 3.627 Å between I(1) and the best plane through the imidazole. I(2) makes close contacts with the hydrogen atoms on C(5) and C(3) of adjacent molecules; iodine–hydrogen distances are H(3A) $(x, y-1, z)$ = 3.34 Å, H(5A) $(-x, -y, -1-z)$ = 3.27 Å, H(5B) $(x, y-1, z)$, and H(5C) $({}^1/_2 - x, -{}^1/_2 + y, -{}^1/_2 - z)$ = 3.28 Å.[42]

The unit cell packing (Figure 7) of the β form (**8**) of the thione **1**–diiodine complex is quite different from that of the α form (**7**).

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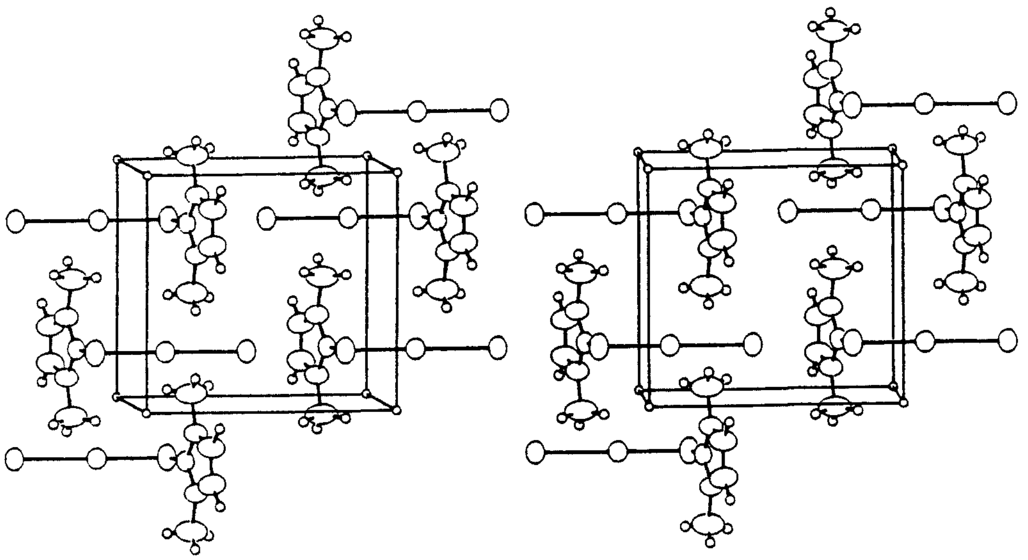

Figure 7. Stereoscopic view of the molecular packing of one crystalline form (β, **8**) of the thione **1**–diiodine charge-transfer complex. View is down the *a* axis; *c* axis is to the right.

In the β form, the molecules form infinite S–I–I–S chains with sulfur–iodine distances of 3.595 Å. This value is considerably shorter than the expected van der Waals radii of 4.00 Å.[43]

The ^{1}H NMR resonances (δ 3.60, 6.75) in free thione **1** are shifted downfield to δ 3.74 and 7.01 in 1:1 complex **7** (α) and to δ 3.70 and 6.88 in 1:1 complex **8** (β). Similarly, the ^{1}H NMR resonance in imidazole-2-thione (δ 6.83) is shifted downfield in the 1:1 charge-transfer complex (δ 7.85), and the ^{1}H NMR resonances in 1-methylimidazole-2-thione [δ 3.51, 6.97 ($J_{4,5}$ = 2.33 Hz), 7.15] are shifted downfield in the 1:1 charge-transfer complex [δ 3.68, 7.47 ($J_{4,5}$ = 2.01 Hz), 7.58].

The ^{13}C NMR resonance observed for the thiocarbonyl group in thione **1** (δ 165.78) is shifted downfield 11 ppm relative to structure **7** (alpha, δ 154.77) and 6.72 ppm upfield relative to structure **8** (beta, δ 159.06). Similar downfield shift trends are observed with imidazole-2-thione (δ 164.39 to 146.08) and 1-methylimidazole-2-thione (δ 165.07 to 149.48). These upfield chemical shifts are consistent with CNDO molecular orbital calculations, which suggest an increased thiocarbonyl carbon shielding in charge-transfer complexes of this type.[44]

The observed incongruity between the appearance of a tricoordinate hypervalent sulfurane (**3**), an ionic molecule (**4**), or a 1:1 thione **1**–diiodine charge-transfer complex in two different crystalline modifications (**7**, **8**) as a function of ligand structure is not solely dependent on ligand electronegativity.[8] It is possible that diiodine is not sufficiently electronegative to stabilize the negatively charged sulfur atom in structure **3** and forms instead a charge-transfer complex (**7** or **8**). The electron-attracting ability of the cyano group also appears to be insufficient to stabilize the hypervalent sulfur in **3**, and ionic compound **4** is formed.[8]

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Elemental analyses were performed by Robertson Laboratory, Madison, NJ 07940.

Mass spectra were obtained on a Finnigan GC/EI-CI mass spectromete with a Nova 3 data system. The percent relative intensities are given in parentheses. Proton NMR and ^{13}C NMR spectra were obtained on a Bruker WM-250 or a GE-Niclet QE-300 spectrometer. The references for ^{13}C NMR spectra are the central solvent (DMSO-d_6) resonances at δ 43.50 and at δ 77.27 (CDCl$_3$), respectively. Infrared spectra were obtained on a Perkin-Elmer 238 spectrometer. Ultraviolet–visible spectra were obtained on Varian Cary 219 spectrophotometer.

Analytical reagent grade dichloromethane was purified by predrying over CaH$_2$ and fractional distillation from CaH$_2$. Analytical grade diiodine was resublimed under reduced pressure.

The appearance of charge-transfer bands was observed in the visible region at constant concentration of diiodine and varying concentrations of thiones (Figure 1) and in the ultraviolet region at constant concentration of thione and varying diiodine concentrations (Figure 2).

Attempts to determine the kinetics of formation of the 1:1 thione–diiodine charge-transfer complexes on a Durrum Model D-110 stopped-flow spectrophotometer was unsuccessful owing to the very rapid rates of reactions.

Imidazole-2-thione was prepared from aminoethanal and potassium thiocyanate as previously described:[45] mp 226–228 °C dec (lit.[45] mp 226–228 °C); IR (KBr pellet) 730, 1070 (C═S), 1230 (—N—C═S, amide I), 1470 (—N—C═S, amide II), 1580 (C═C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.83; ^{1}H NMR (D$_2$O) δ 6.32; ^{13}C NMR (DMSO-d_6) δ 119.81, 164.39; UV (CH$_2$Cl$_2$) λ_{max} 270 nm (log ϵ 4.1); CIMS *m/z* 101 ([MH]$^+$, 100), 100 ([MH$^+$ − H], 30.3); EIMS *m/z* 100 ([M]$^+$, 100), 73 ([M$^+$ − HCN], 14.7).

1-Methylimidazole-2-thione is commercially available:[46] mp 144–147 °C; IR (KBr pellet) 735, 760, 1085 (C═S), 1150 (C—N), 1250 and 1280 (—N—C═S, amide I), 1340 (CH$_3$), 1460 (—N—C═S, amide II), 1580 (C═C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.51, 6.97 ($J_{4,5}$ = 2.33 Hz), 7.15; ^{13}C NMR (DMSO-d_6) δ 37.56, 118.07, 123.47, 165.07; UV (CH$_2$Cl$_2$) λ_{max} 272 nm (log ϵ 4.21); CIMS *m/z* 115 ([MH$^+$], 100); EIMS *m/z* 114 ([M]$^+$, 100), 81 ([M$^+$ − SH], 13.4), 72 (23.5).

1,3-Dimethylimidazolium iodide was prepared as previously described.[4–6,47] Imidazolium iodide salt: mp 87–89 °C (lit.[47] mp 81–83 °C); ^{1}H NMR (CDCl$_3$) δ 3.87 (s, 6 H), 7.69 (d, 1 H), 7.71 (d, I H), 9.08 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 39.88, 127.10, 140.73.

1,3-Dimethylimidazole-2-thione (1) was prepared from 1,3-dimethylimidazolium iodide as previously described.[4–6] Thione **1**: mp 183–184 °C (lit.[6] mp 183–184 °C); IR (KBr pellet) 730, 1070 (C═S), 1170 (C—N), 1240 (—N═C═S, amide I), 1390 (CH$_3$), 1470 (—N—C═S, amide II), 1560 (C═C); ^{1}H NMR (DMSO-d_6) δ 3.60 (s, 6 H), 6.75 (s, 2 H); ^{13}C NMR δ 38.47, 122.0; 165.78; UV (CH$_2$Cl$_2$) λ_{max} 267 nm (log ϵ 4.21); CIMS *m/z* 129 ([MH]$^+$, 100); EIMS *m/z* 128 ([M]$^+$, 100), 95 ([M$^+$ − SH], 16.8).

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Preparation of the 1,3-Dimethylimidazole-2-thione (1) Charge-Transfer Complex. Crystal Modification 7 (α). To a 125-mL Erlenmeyer flask containing 0.128 g (10 mmol) of the thione **1** in 25 mL of dry dichloromethane was added a solution of diiodine (0.254 g, 10 mmol in 25 mL of dichloromethane). The reaction mixture was stirred 30 min, and the solvent was removed in vacuo (30–50 Torr). Dark red-orange charge-transfer complex **7** (α): mp 100–101 °C dec; IR (KBr pellet) 820, 1000 (C=S), 1170 (C—N), 1280 (—N—C=S amide I), 1390 (CH_3), 1490 (—N—C=S, amide II), 1640 (C=C), 2800 (C—H), 3000 (C—H) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.74, 7.01; ^{13}C NMR (DMSO-d_6) δ 39.37, 125.18, 154.77; UV (CH_2Cl_2) λ_{max} 350 nm; CIMS m/z 129 ([thione H]$^+$, 100); EIMS m/z 128 ([thione]$^+$, 100), 254 ($[I_2]^+$, 86.3), 127 ([I]$^+$ 59.5), 95 ([thione − SH]$^+$, 21.2). Anal. Calcd for $C_5H_8I_2N_2S$: C, 15.72; H, 2.11; I, 66.44; N, 7.33; S, 8.39. Found: C, 15.99; H, 2.00; N, 7.10; S, 8.29.

Crystals of the thione **1**–diiodine charge-transfer complex **7** were grown by the method of liquid diffusion. The solid complex **7** was dissolved in 5 mL of dichloromethane and filtered through a glass filter plug into a dry dust-free 30-mL test tube, and petroleum ether (bp 37–57 °C, 20 mL) was carefully layered on top of the dichloromethane solution. An immediate turbidity formed at the solvent interface. The crystals of complex **7** (α) were collected after 24 h.

Preparation of the 1,3-Dimethylimidazole-2-thione (1)–Diiodine Charge-Transfer Complex. Crystal Modification 8 (β): To a 125-mL Erlenmeyer flask containing 0.128 g (10 mmol) of thione **1** in 25 mL of dry CH_2Cl_2 was added a solution of 0.127 g (5 mmol) of diiodine in 25 mL of dry CH_2Cl_2. The solution was stirred for 30 min, and the solvent was removed in vacuo (30–50 Torr) to give a 2:1 thione **1**–diiodide complex (cf. **10**). 2:1 thione **1**–diiodide complex: mp 105~106 °C dec; IR (KBr pellet) 740, 1180 (C—N), 1230 (—N—C=S amide I), 1390 (CH_3), 1430 (—N—C=S amide II), 1680 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.70, 6.88; ^{13}C NMR (DMSO-d_6), δ 39.07, 124.08, 159.06; UV (CH_2Cl_2) λ_{max} 350, 500 nm; CIMS m/z 129 ([thione H]$^+$, 100); EIMS m/z 128 ([thione]$^+$, 100), 254 ($[I_2]^+$, 33.3), 127 ([I]$^+$, 31.7), 95 ([thione − SH]$^+$, 18.3). Anal. Calcd for $C_{10}H_{16}I_2N_4S_2$: C, 23.54; H, 3.16; N, 10.98; S, 12.57. Found: C, 23.59; H, 2.92; N, 100.79; S, 12.59.

The 2:1 thione **1**–diiodide complex (100 mg) was dissolved in dry CH_2Cl_2 (5 mL) and filtered through a glass filter plug into a dry dust-free 30-mL test tube. Petroleum ether (bp 37–57 °C, 20 mL) was carefully layered on top of the dichloromethane solution. After 48 h the solvents became homogeneous and crystals had formed at the initial solvent interface. The solvent was decanted from the crystals and then set aside. An X-ray structure determination of these crystals showed them to be a second crystalline modification (β, **8**) of charge-transfer complex **7** (α).

The solvent, which was decanted from the crystals, was removed in vacuo to give crude residue of thione **1** (mp 177–180 °C). Recrystallization of the crude crystals from acetone gave pure thione **1** (mp 182–183 °C).

The 1:1 Imidazole-2-thione–Diiodine Charge-Transfer Complex was prepared as described above for the preparation of the thione **1**–diiodine complex **7** (α). Charge-transfer complex: mp 134–136 °C dec; IR (KBr pellet) 740, 1080 (C=S), 1130 (—N—C=S, amide I), 1410 (—N—C=S, amide II), 1580 (C=C); ^{1}H NMR (DMSO-d_6) δ 7.85; ^{13}C NMR (DMSO-d_6) δ 125.38, 146.08; UV (CH_2Cl_2) λ_{max} 300 nm; CIMS m/z 101 ([thione H]$^+$, 100), EIMS m/z 100 ([thione]$^+$, 100), 254 ($[I_2]^+$, 29.3), 127 ([I]$^+$, 20.6). Anal. Calcd. for $C_3H_4I_2N_2S$: C, 10.18; H, 1.14; N, 7.91; S, 9.06. Found: C, 10.41; H, 0.99; N, 8.13; S, 9.15.

The bis(imidazole-2-thione)iodine(I) iodide (2:1 complex 10) was prepared from imidazole-2-thione and diiodine as described above. Red-purple crystals: mp 172–174 °C dec; IR (KBr disk) 760, 1080 (C=S), 1100, 1120 (C—N), 1250 (—N—C=S, amide I), 1300, 1570 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.74; ^{13}C NMR (DMSO-d_6) δ 123.07, 152.73; UV (CH_2Cl_2) λ_{max} 300 nm; CIMS m/z 101 ([thione H]$^+$, 100), 71 (30); EIMS m/z 100 ([thione]$^+$, 100), 254 ($[I_2]^+$, 51), 127 ([I]$^+$, 25). Anal. Calcd. for $C_6H_8I_2N_4S_2$: C, 15.87; H, 1.77; N, 12.33; S, 14.12. Found: C, 15.74; H, 1.54; N, 12.13; S, 14.01.

The 1:1 1-methylimidazole-2-thione–diiodine charge-transfer complex was prepared as described above for complex **7** (α). Liquid purple charge-transfer complex: IR (KBr pellet) 730, 1090 (C=S), 1160 (C—N), 1285 (—N—C=S, amide I), 1350 (CH_3), 1450 and 1470 (—N—C=S, amide II), 1575 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.68, 7.47, 7.58 ($J_{4,5}$ = 2.01 Hz); ^{13}C NMR (DMSO-d_6) δ 38.73, 123.52, 128.11, 149.48; CIMS m/z 115 ([thione H]$^+$, 100), 83 ([MH$^+$ − SH], 15.3); EIMS m/z 254 ($[I_2]^+$, 100), 127 ([I]$^+$, 43.8); 114 ([thione]$^+$, 76.1), 81 ([thione − SH]$^+$, 10.1). Anal. Calcd. for $C_4H_6I_2N_2S$: C, 13.06; H, 1.64; N, 7.61; S, 8.71. Found: C, 13.19; H, 1.59; N, 7.45; S, 8.55.

The bis(1-methylimidazole-2-thione)iodine(I) iodide (2:1 complex 10) was prepared from 1-methylimidazole-2-thione and diiodine as described above. Yellow-red crystals: mp 108–110 °C dec; IR (KBr disk) 770, 1100 (C=S), 1170 (C—N), 1270 and 1300, (—N—C=S, amide I), 1370 (CH_3), 1490 (—N—C=S), 1570 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 38.43, 120.56, 125.69, 156.82; UV (CH_2Cl_2) λ_{max} 300, 350 nm; CIMS m/z 115 ([thione H]$^+$, 100), 83 ([thione − SH]$^+$, 11.5); EIMS m/z 114 ([thione]$^+$, 100), 127 ([I]$^+$, 34), 254 ($[I_2]^+$, 85). Anal. Calcd. for $C_{H12}I_2N_4S_2$: C, 19.93; H, 2.51; N, 11.61; S, 13.30. Found: C, 20.18; H, 2.28; N, 11.68; S, 13.01.

Acknowledgment is made to the National Science Foundation for support of this research (Grant CHE 86-19651) and for purchase of the stopped-flow spectrophotometer (Grant CHE 77-04790) and to the National Science Foundation Instrumentation Program for financial assistance toward the purchase of the NMR spectrometers (Grant CHE 85-11705). Funds for the purchase of the Nicolet P3 diffractometer system and MicroVAX II computer and upgrade of the Syntex $P2_1$ diffractomer were made available by the NSF Chemical Instrumentation program under Grant CHE-85-14495.

Supplementary Material Available: Descriptions of the X-ray diffraction studies and structure solutions and tables of final atomic coordinates, intermolecular distances and angles, and anisotropic thermal parameters (7 pages); tables of observed and calculated structure factors (23 pages).[48–55] Ordering information is given on any current masthead page.